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THE CHEMICAL SOCIETY.

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ON
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1908. Vol. XCIV. Part I.

LONDON:
GURNEY & JACKSON, 10, PATERNOSTER ROW.
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REPORT OF

THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society :

Government Laboratory,
Clement's Inn Passage,
Strand, London, W.C.
29th October, 1908.

Gentlemen,

I beg to forward you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1909, to which I have affixed, as desired by them, the signatures of Professors Ostwald and Urbain.

The general revision of the values of the atomic weights of the elements, based on the fundamental values for hydrogen, nitrogen, the halogens, silver, etc., as ascertained by the laborious and accurate determinations which have been made in various laboratories during recent years, and to which reference was made in preceding Reports, has now been completed and the Table submitted with the present Report embodies the results of the re-calculations. A number of atomic weights are shown to be slightly influenced by the adoption of the new values, but the changes thus introduced are, it must be admitted, less profound than was generally anticipated. Certain of the values still remain affected by errors far larger than those introduced by the selection of a particular fundamental value of the element with which comparison is made.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.

Report of the International Committee on Atomic Weights, 1909.

Since the publication of our last Report, several important memoirs upon atomic weights have appeared containing data of fundamental significance. They may be summarised as follows :

Hydrogen.—W. A. Noyes (*J. Amer. Chem. Soc.*, 1907, **29**, 1718) has made complete syntheses of water in five series of determinations. The first series, however, was defective, and is therefore not published by the author. In mean, the four successful series give H = 1·00787, as compared with Morley's figure, 1·00762. The general mean of these values, combined with all other trustworthy determinations, is 1·00779. The rounded-off value, 1·008, is therefore retained in the table.

Chlorine.—Noyes and Weber (*J. Amer. Chem. Soc.*, 1908, **30**, 13) have effected the synthesis of hydrochloric acid, weighing the hydrogen in palladium, the chlorine in potassium chloroplatinate, and also the hydrochloric acid produced by the union of the two elements. From the ratio H : Cl, Cl = 35·458, when H = 1·00779. From the ratio H : HCl, Cl = 35·457.

The same ratios have also been measured by Edgar (*Proc. Roy. Soc.*, 1908, **81**, *A*, 216), but by a different method. The hydrogen, as in former determinations, was weighed in palladium, but the chlorine was prepared by the electrolysis of fused silver chloride, and weighed in the liquid form. The hydrogen chloride was weighed directly in three experiments, and in two others after absorption in water. From the ratio H : Cl, Cl = 35·468. From the ratio H : HCl, Cl = 35·467. With Morley's value for H, the results are nearer Cl = 35·46. Taking all the data together, the value Cl = 35·46 seems to be as near the truth as can be positively asserted now. This includes the former work of Dixon and Edgar, and the density determinations by Guye and Gazarian.

*Sulphur.**—From eighteen determinations of the density of hydrogen sulphide, Baume and Perrot deduce the value S = 32·070. In an earlier investigation by Baume,† who determined the density of sulphur dioxide, he found lower values for S. The figure 32·07, however, is in close agreement with the value obtained by Richards and Jones, when Ag = 107·88, and is doubtless very nearly true.

Lead.—Atomic weight determined by Baxter and Wilson (*Proc. Amer. Acad.*, **43**, 365) from analyses of the chloride. With Ag = 107·93, Pb = 207·19. With Ag = 107·88, Pb = 207·10. This value is still much higher than that previously accepted.

Cadmium.—Blum (*Thesis*, University of Pennsylvania, 1908) has attempted to determine the atomic weight of cadmium by conversion of the oxide into the sulphide. The values obtained range from 112·50 to 112·88, and are admittedly of slight significance.

Tellurium.—In an elaborate memoir upon the atomic weight of tellurium, Baker and Bennett (Trans., 1907, **91**, 1849) give determinations by two new methods. By heating tellurium dioxide with sulphur in such a way that only sulphur dioxide could escape, the ratio TeO_2 to SO_2 was determined. From the mean of twenty-five determinations, Te = 127·609. By direct conversion of tellurium into the tetrabromide, the mean of eighteen determinations was Te = 127·601, when Br = 79·96. Referred to Br = 79·92, this becomes 127 = 54. Several analyses of tellurium tetrachloride, for which the details are not published, gave values for Te between 127·58 and 127·64. On the basis of the modern values for Ag, Cl, and Br, and with due regard to the earlier work of Pellini, Gutbier, Koethner, Norris, Scott, Staudenmaier, and others, the rounded-off figure, Te = 127·5, seems to be fairly acceptable.

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* Private communication from Prof. P. A. Guye.

† *J. Chim. Phys.*, 1908, **6**, 1. Baume also determined the densities of methyl oxide and methyl chloride.

Marckwald,* however, by careful dehydration of telluric acid, found values for Te ranging from 126·65 to 126·94. Six experiments were made, the mean of five, rejecting the lowest of all, being Te = 126·85. This falls below the atomic weight of iodine, and is therefore in harmony with the periodic classification. In view of the general agreement between other investigators in favour of a higher figure, Marckwald's work cannot be accepted without confirmation. The controversy over tellurium is evidently not ended.

Rhodium.—Hüttlinger (*Diss.*, Erlangen, 1907), working in Gutbier's laboratory, made three reductions in hydrogen of rhodium pentamine chloride. His results, which seem to be preliminary in character, are practically identical with those obtained by Seubert and Kobbe, whose value for rhodium has been accepted since 1890. No change in this atomic weight is needed.

Palladium.—Woernle (*Sitzungsber. phys. med. Soz. Erlangen*, **38**, 296) made seven analyses of palladosamine chloride: two by reductions in hydrogen, three electrolytically. The mean value obtained was Pd = 106·708, presumably computed with the old figures for N and Cl.

Haas (*Diss.*, Erlangen, 1908), from similar reductions of palladosamine bromide, found Pd = 106·75, calculated with N = 14·037 and Br = 79·953. These determinations, like those of Krell, were made under the direction of Professor Gutbier. The results obtained by Krell, Woernle, and Haas agree well together, and also with Amberg's determinations, and are probably quite accurate. Recomputed, with modern values for N and Cl, Pd = 106·7 very nearly, with an uncertainty of not over 0·05.

Lower values were found by Kemmerer (*Thesis*, University of Pennsylvania, 1908), working under Professor Edgar F. Smith. By reduction in hydrogen, palladosamine chloride gave Pd = 106·399 and 106·442 as the means of two series of observations. From palladosamine cyanide the value Pd = 106·458 was obtained. The mean of fifteen determinations, taken as one series, gave Pd = 106·434. The more concordant values cited above seem to be more trustworthy, at least so far as present evidence permits us to judge. Kemmerer's computations were made with N = 14·01 and Cl = 35·473.

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* *Ber.*, 1907, **40**, 4730. For a criticism of Marckwald, see Baker, *Chem. News*, 1908, **97**, 209.

Europium.—From analyses of the octahydrated sulphate, Jantsch (*Compt. rend.*, 1908, **146**, 473) finds Eu = 152·03, when S = 32·06 and H = 1·008. The round number 152 is retained in the table. This is probably the nearest significant figure.

Erbium.—By repeated fractionation of erbium compounds, Hofmann and Burger (*Ber.*, 1908, **41**, 308) have isolated an oxide of slightly higher molecular weight than that of the old erbia. To the new metal thus indicated they assign the name "neo-erbium," and by synthesis of the sulphate they find its probable atomic weight to be 167·43. The rounded-off figure 167·4 is given provisionally in the table, to stand until more complete data have been obtained.

Ytterbium.—That the old ytterbium is a mixture of two elements has been proved by Urbain (*Compt. rend.*, 1907, **145**, 759, November 4, 1907. See also *Compt. rend.*, 1908, **146**, 406, and *Chem. Zeit.*, 1908, **32**, 730), in Paris, and Auer von Welsbach,* in Vienna, working almost simultaneously and independently. In his earlier paper, Urbain names the two elements "neoytterbium" and "lutecium," with approximate atomic weights of 170 and 174 respectively. In his second memoir, Urbain gives atomic weights for a series of ytterbium fractionations, ranging from 170·6 to 174·02. Welsbach, whose work appeared later than Urbain's, names the two elements "aldebaranium," atomic weight 172·90, and "cassiopeium," atomic weight 174·23. Since Urbain has clear priority, his nomenclature should be preferred, but the atomic weights need to be more sharply determined. Incidentally, Urbain notes that the atomic weight of thulium is lower than 168·5.

Columbium.—A concordant series of determinations made under the direction of Edgar F. Smith † give columbium an atomic weight of 93·5. This is lower than the value hitherto accepted.

Radium.—Thorpe (*Proc. Roy. Soc.*, 1908, **80**, *A*, 298) has redetermined the atomic weight of radium by analyses of the chloride. In mean his determinations, calculated with Ag = 107·88 and Cl = 35·46, give Ra = 226·64. Thorpe, however, gives preference to the determinations by Mme. Curie, who worked with larger quantities of material, regarding his own work as confirmatory. The recalculated value is 226·4.

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* *Monatsh.*, **29**, 181, Feb., 1908. Read before the Vienna Academy, Dec. 19, 1907.

† Private communication. The details are shortly to be published.

In their Report for 1908 this Committee recognised the fact that a general revision of the atomic weight table was desirable, and such a revision has now been made. Modern investigations have shown that the fundamental values required modification, and through them many other atomic weights are affected, although the changes thus brought about are less important than they were generally supposed to be. Many atomic weights remain practically unaltered, and in few instances are the changes large, as a comparison of the new table with its predecessors will show. A careful scrutiny of all the evidence was, however, none the less necessary, and the table now offered gives the results thus obtained.

The fundamental atomic weights, the standards of reference employed in the calculations, are as follows; when O = 16.

H,	1·008.	Br,	79·916.
C,	12·00	Ag,	107·880.
N,	14·007.	K,	39·095.
Cl,	35·460.	S,	32·070.

The value for silver is possibly a trifle too low, by from three to five units in the third decimal place. A combination of the best measurements gives Ag = 107·883. In this case, and in others as well, the second place of decimals is given in the table, the third place being uncertain. Thus we have K, 39·10, N, 14·01, Br, 79·92, &c. Only with hydrogen is the third place retained.

In adjusting the other atomic weights, the determinations by Richards* and his colleagues have generally been given preference. They are certainly entitled to the highest weight, but probably not to exclusive consideration. The work of Guye and his associates at Geneva, and the recent direct measurements of the chlorine-hydrogen ratio are also of very great importance. It is to work of this order that we must look for ultimate precision. Important investigations upon atomic weights are now being carried out in several laboratories, and our knowledge of these constants will doubtless become much more exact within the near future.

(Signed) F. W. CLARK,
W. OSTWALD,
T. E. THORPE,
G. URBAIN.

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* An excellent summary of the Harvard work is given by Richards in *J. Chim. Phys.*, 1908, **6**, 92.

1909.

International Atomic Weights.

		O=16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	75·0
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·09
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·1
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·4
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·0
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·85
Krypton	Kr	81·8
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	7·00
Lutecium	Lu	174
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20
Nickel	Ni	58·68
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·0
Platinum	Pt	195·0
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·62
Sulphur	S	32·07
Tantalum	Ta	181·0
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·42
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·2
Xenon	Xe	128
Ytterbium (Neoytterbium)	Yb	172
Yttrium	Y	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.

2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.

3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.

4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.

5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.

6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.

7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.

8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.

9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

10. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

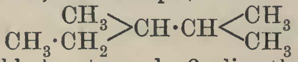
11. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulæ*.

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

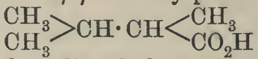
14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2I$ α-iodobutane, $CH_3\cdot CH_2\cdot CH_2\cdot CN$ α-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,



$$\begin{matrix}CH_3\\CH_3\cdot CH_2\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} \quad \text{or} \quad CH_3\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_3$$

should be termed $\beta\gamma$-dimethylpentane, not methylethyl*iso*propylmethane, and



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\CO_2H\end{matrix} \quad \text{or} \quad CH_3\cdot CHMe\cdot CHMe\cdot CO_2H$$

should be termed $\alpha\beta$-dimethylbutyric acid, not $\alpha\beta\beta$-trimethylpropionic, or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

16. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3\cdot[CH_2]_5\cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α-ethoxypropionic acid, $OEt\cdot CHMe\cdot CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3\cdot CO_2H$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $OAc\cdot CHMe\cdot CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $C_6HEt_2(OH)_2\cdot CO_2H$, and not $C_6H_3(OEt)_2\cdot CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2\cdot CO_2H$.

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid, $NH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, β-anilino-acrylic acid, $NHPh\cdot CH{:}CH\cdot CO_2H$, α-iminopropionic acid, $NH{:}CMe\cdot CO_2H$.

22. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 3rd decade (1893–1902) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

25. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$.

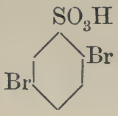
(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

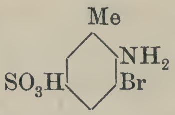
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—

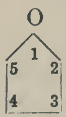


is 2 : 5-dibromobenzenesulphonic acid ;

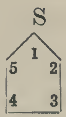


is 3-bromo-*o*-toluidine-5 sulphonic acid.

29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (2nd edition, 1899, pp. 16—26) should be used, of which the following schemes may be regarded as typical :—



Furan.



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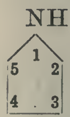

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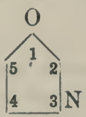

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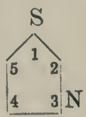

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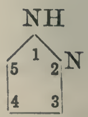

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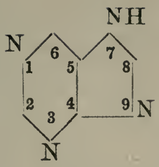
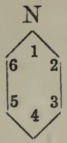
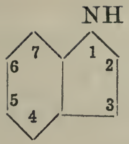


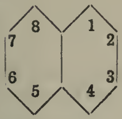
Purine.*



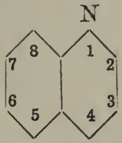
Pyridine.



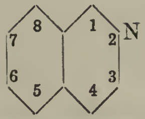
Indole.



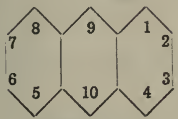
Naphthalene.



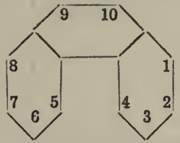
Quinoline.



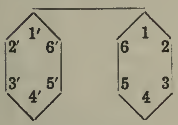
*iso*Quinoline.



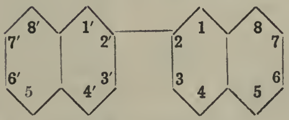
Anthracene.



Phenanthrene.



Diphenyl.



ββ-Dinaphthyl.

Manuscript.

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

34. Abstractors are expected to read and correct proofs carefully, and to check all formulæ and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

⁂ The Editor's decision, in all matters connected with the Abstracts, must be considered final.

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* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon.*

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. Soc. chim.* 1901, [iii], **25**, 794; *Gazzetta* 1901, **31**, i, 554.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. chem. Physiol. Path.	Beiträge für chemische Physiologie und Pathologie.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
* *Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci., St. Pétersbourg.	Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Coll. Agr. Tōkyō	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Zentr.*	Chemisches Zentralblatt.

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* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

Abbreviated Title.	Journal.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. phys.	Journal de Chimie physique.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique	Journal de Physique.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
K. Svenska Vet-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Lancet.	The Lancet.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Eng. Kyōtō.	Memoirs of the College of Science and Engineering Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Metallurgie	Metallurgie.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Pflüger's Archiv.	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Rev.	Pharmaceutical Review.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.
Pharm. Zentr-h.	Pharmazeutische Zentralhalle.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. exp. Physiol.	Quarterly Journal of experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. de Métallurgie	Revue de Métallurgie.
Rev. intern. Falsif.	Revue internationale des Falsifications.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Mining Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie der Kolloide.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Farb.-Ind.	Zeitschrift für Farben-Industrie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Photograph. Photophysik. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitsch. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Development of Organic Chemistry in the Last Forty Years. Carl Graebe (*Ber.*, 1907, 40, 4638—4644).—A lecture delivered before the German Chemical Society. W. H. G.

Fractional Distillation of Higher Normal Paraffins from Lignite in the Vacuum of the Cathode Light. Friedrich Krafft (*Ber.*, 1907, 40, 4779—4784).—An examination of a Saxon paraffin wax of a complicated character. The apparatus used consists essentially of a small flask for distillation provided with a long neck in which the thermometer bulb can be immersed in the liquid or vapour at will; for details, the original should be consulted. The first fractionation of 450 grams resulted in the collection of five fractions, and each fraction was carefully redistilled. After repeated fractionation, the following eighteen hydrocarbons were isolated and their molecular weights by the boiling-point method determined.

		B. p., 0 mm.	M. p.	*D* liquid.
$C_{19}H_{40}$	Nonadecane	109·0°	31·8—32·0°	—
$C_{20}H_{42}$	Icosane	117·5	36·3—36·6	0·7775
$C_{21}H_{44}$	Heneicosane.........	125·5	39·9—40·2	0·7778
$C_{22}H_{46}$	Docosane	130·5	44·0—44·5	0·7776
$C_{23}H_{48}$	Tricosane	138·0	47·2—47·5	0·7799
$C_{24}H_{50}$	Tetracosane	145·5	50·7—51·3	0·7781
$C_{25}H_{52}$	Pentacosane	152·5	53·8—54	0·7785
$C_{26}H_{54}$	Hexacosane	160	56·8—57	0·7787
$C_{27}H_{56}$	Heptacosane	167	about 59·4	0·7789
$C_{28}H_{58}$	Octacosane	173·5	,, 61·6	0·7792
$C_{29}H_{60}$	Nonacosane	179	63·6—64·1	0·7797
$C_{30}H_{62}$	Triacontane	186	65·6	0·7797
$C_{31}H_{64}$	Hentriacontane ...	193·5	68·4	0·7799
$C_{32}H_{66}$	Dotriacontane	201	69·8	0·7798
$C_{33}H_{68}$	Tritriacontane	208	71·8	0·7801
$C_{34}H_{70}$	Tetratriacontane ...	215	about 73	0·7806
$C_{35}H_{72}$	Pentatriacontane...	222	,, 74	0·7813
$C_{36}H_{74}$	Hexatriacontane about	230	,, 76	0·7819

There is a series of still higher homologues present in this paraffin, b. p. 250—290°/0 mm., and a portion boiling above 300°, the hydrocarbons of which must contain at least fifty carbon atoms. W. R.

Electro-Syntheses [with Ethylene and Acetylene]. Sima M. Losanitsch (*Ber.*, 1907, **40**, 4656—4666).—See this vol., ii, 32.

Isomeric Change of *iso*Butyl Alcohol Effected by Nitrous Acid. Louis Henry (*Compt. rend.*, 1907, **145**, 899—902).—The isomeric change which certain aliphatic amines undergo when their salts are treated with metallic nitrites has been examined in the cases of *n*-propylamine (Meyer and Forster, Abstr., 1876, 543) and ββ-dimethylpropylamine (Tissier, Abstr., 1891, 998; Freund and Lenze, Abstr., 1891, 1172); in the first case, a mixture of *n*- and *iso*-propyl alcohols is obtained containing 58% of the secondary alcohol, whilst in the second case the tertiary alcohol, dimethylethylcarbinol, is the sole product of the reaction. The author has extended the investigation to the intermediate homologue, *iso*butylamine, and finds that on treatment with sodium nitrite in a slightly acid solution it is converted into a mixture of *iso*butyl alcohol and trimethylcarbinol, of which 75% is the tertiary alcohol. These three amines contain respectively the groupings: $-CH_2\cdot CH_2\cdot NH_2$, $>CH\cdot CH_2\cdot NH_2$, and $\geqslant C\cdot CH_2\cdot NH_2$, and the results show that when they are converted into alcohols by the action of nitrous acid they suffer a partial or complete isomeric change, whereby the resulting alcohol has the hydroxyl attached to that carbon atom which in the original compound was associated with the least number of hydrogen atoms. M. A. W.

Action of Magnesium Organic Compounds on Tiglic Aldehyde. Paul Abelmann (*Ber.*, 1907, **40**, 4589—4590).—*γ-Methyl-Δ^γ-pentene-β-ol*, $CHMe:CMe\cdot CHMe\cdot OH$, obtained from magnesium methyl bromide and tiglic aldehyde, is a colourless liquid, b. p. 139—141°. Its *acetate*, $C_8H_{14}O_2$, has b. p. 153—155°.

δ-Methyl-Δ^δ-hexene-γ-ol, $CHMe:CMe\cdot CHEt\cdot OH$, obtained from magnesium ethyl bromide and tiglic aldehyde, has b. p. 154—155°/80 mm. Its *acetate*, $C_9H_{16}O_2$, has b. p. 167—170°.

γη-Dimethyl-Δ^β-octene-δ-ol, $CHMe:CMe\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CHMe_2$, obtained from magnesium *iso*amyl bromide and tiglic aldehyde, has b. p. 202—204°. A. McK.

Esterification of Phosphoric Acid by Glycerol. Georges Prunier (*Bull. Soc. chim.*, 1907, [iv], **1**, 1046—1048).—The rate of esterification of phosphoric acid by glycerol has been investigated under varying conditions of concentration, temperature (110°, 130°, or 150°), and pressure, and the nature of the products determined.

The results show that care must be taken to eliminate water as it is formed, and this may be accomplished by heating the reaction mixture under reduced pressure or by exposing a comparatively large evaporating surface.

The limit appears to be reached when 80% of the acid is esterified, and this point is arrived at more quickly at the higher temperatures. The extent to which esterification proceeds is increased as the concentration of alcohol and acid is increased and as the time of operation is extended. At atmospheric pressure, the best result (78%) is obtained at 110° and using 60% phosphoric acid and glycerol of 60°B.

At the higher temperatures and under reduced pressure, the chief product is the di-ester, this being replaced, in part, by the mono-ester when esterification is slow (namely, at higher pressures and lower temperatures), and by the tri-ester when the operation is conducted at a still higher temperature. No method is yet available for the separation of the mono- from the di-ester. Mercurous and mercuric glycerophosphates have been prepared for the first time. T. A. H.

Action of Sodium Ethoxide on Trichloromethylsulphonyl Chloride. ALEXANDER CRUM BROWN and THOMAS F. COWIE (*Proc. Roy. Soc. Edin.*, 1907, **27**, 369—370).—The action of an ethereal solution of trichloromethylsulphonyl chloride on sodium ethoxide results in the production of ethyl ether, sodium chloride, sodium carbonate, sodium sulphite, and small quantities of ethyl carbonate, ethyl orthocarbonate, and sodium ethyl sulphite. The most probable explanation of the reaction, which also takes place when solutions of the two compounds in absolute alcohol are mixed, is that the ester $C(OEt)_3{\cdot}SO_2{\cdot}OEt$ is formed, and acted on by sodium ethoxide, thus: $C(OEt)_3{\cdot}SO_2{\cdot}OEt + NaOEt = C(OEt)_4 + NaSO_2{\cdot}OEt$ or $CO(OEt)_2 + OEt_2 + NaSO_2{\cdot}OEt$. Further action of sodium ethoxide on the carbonic esters and sodium ethyl sulphite results in the formation of ether, sodium carbonate, and sodium sulphite. W. H. G.

Complex Iridium Salts. Irido-oxalates. CESARE GIALDINI (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 648—655. Compare Abstr., 1907, i, 1005).—*Silver irido-oxalate*, $Ag_3Ir(C_2O_4)_3,3H_2O$, prepared from the corresponding potassium salt and silver nitrate, forms silky, yellow needles, exploding at 145—150°, and exhibits cryoscopic behaviour in water, indicating that it undergoes dissociation into three Ag ions and the complex ion: $Ir(C_2O_4)_3$.

The *pyridine* salt, $(C_5H_6N)_3Ir(C_2O_4)_3,3H_2O$, and the *barium* salt, $Ba_3[Ir(C_2O_4)_3]_2$, were also prepared.

Salts of the type $M'''R(C_2O_4)_2$, such as are formed by tervalent iron, aluminium, and chromium, do not appear to be formed with iridium. T. H. P.

Acids of High Melting Point in Japanese Wax, in Particular, Nonadecamethylenedicarboxylic Acid. RICHARD SCHAAL (*Ber.*, 1907, **40**, 4784—4788).—Eberhardt's acid, m. p. 117·5°, from Japan wax has the composition $C_{21}H_{40}O_4$ (*Diss. Strasburg*, 1888; compare also Geitel and van der Want, Abstr., 1900, i, 271). The acids in Japan wax, when carefully fractionated in the vacuum of the cathode light, give dicarboxylic acids of high m. p. After recrystallisation from 75% methyl alcohol and redistillation in a vacuum, two fractions are obtained of b. p. 180—210° and 210—245°/0 mm. and m. p. 98—100°

and 107—112° respectively. From the latter fraction, Eberhardt's acid was isolated; the *silver* salt, $C_{21}H_{38}O_4Ag_2$, *ethyl* ester, $C_{21}H_{38}O_4Et_2$, m. p. 53°, and *diamide*, $C_{21}H_{38}O_4(NH_2)_2$, m. p. 174—175°, were prepared. The acid has been identified as n-*nonadecamethylenedicarboxylic acid*, $CO_2H{\cdot}[CH_2]_{19}{\cdot}CO_2H$, by converting the acid into *n*-nonodecane by baryta. From the fraction of b. p. 180—210° by repeated fractionation and treatment with baryta, *n*-octadecane and *n*-heptadecane have been identified, thus establishing the presence of the two lower homologues of nonadecamethylenedicarboxylic acid.

W. R.

Syntheses of *r*-Erythric Acid and of Inactive Erythritol. Robert Lespieau (*Bull. Soc. chim.*, 1907, [iv], 1, 1112—1120).—The syntheses were effected as already described (Abstr., 1904, i, 471; 1905, i, 566; 1907, i, 173), but fuller details are now given of the methods employed and further data regarding some of the substances obtained. *r*-Erythrolactone is soluble in water or alcohol, insoluble in ether, and does not boil even under reduced pressure (20 mm.) without decomposition. It forms, from acetone, large monoclinic prisms [$a:b:c = 1{\cdot}6886:1:1{\cdot}1394$; $\beta = 92°53'$] (measurements by Wyrouboff). The *hydrazide* of the corresponding acid has m. p. 145—146°, and the *brucine* salt has m. p. 210° (decomp.). These figures differ considerably from those recorded for corresponding compounds of the *d*-acid recorded by Ruff (Abstr., 1900, i, 139).

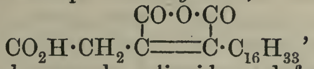
A yield of 30% of the theoretical of inactive erythritol is obtained under the conditions already described (Abstr., 1907, i, 173), but varied by using a large excess of sodium amalgam (fifty times the weight of the erythrolactone employed).

It is pointed out that the formation of inactive erythritol from *r*-erythrolactone probably takes place in the same manner as the production of *i*-tartaric acid from maleic acid.

T. A. H.

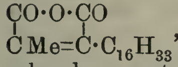
Agaricic Acid. Hermann Thoms and J. Vogelsang (*Annalen*, 1907, **357**, 145—170).—A résumé is given of the work of previous authors on agaricic acid. It is now found that, contrary to Jahn's statement (Abstr., 1884, 354), agaricic acid is a tribasic hydroxy-acid and has the formula: $C_{22}H_{40}O_7,1\frac{1}{2}H_2O$, $[\alpha]_D - 8{\cdot}84°$, and loses $1\frac{1}{2}H_2O$ on prolonged heating at 100°; the *potassium* salt has $[\alpha]_D - 9{\cdot}82°$. The *trimethyl* ester, $C_{25}H_{46}O_7$, crystallises in needles, m. p. 63—64°. The triethyl ester, $C_{28}H_{52}O_7$, crystallises in needles, m. p. 36—37° (Siedler and Winzheimer, Abstr., 1902, i, 487). These esters form only oily acetyl derivatives. *Methyl benzoylagaricate*, $OBz{\cdot}C_{19}H_{36}(CO_2Me)_3$, prepared by heating the trimethyl ether with benzoyl chloride at 170°, forms colourless crystals, m. p. 39—40°. On hydrolysis with boiling alcoholic potassium hydroxide, the esters yield agaricic acid, which is partly decomposed, yielding stearic acid; this is formed also by heating agaricic acid with alcoholic potassium hydroxide at 150—160°. The action of hot concentrated sulphuric acid on agaricic acid leads to the formation of methyl heptadecyl ketone (Krafft, Abstr., 1880, 34), which forms an *oxime*, $C_{19}H_{39}ON$, m. p. 76—77°.

When heated in a current of hydrogen at 140° for six hours, agaricic acid yields the amorphous *anhydride*,



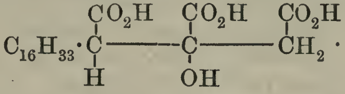
$$\begin{array}{l} \qquad\qquad\quad \mathrm{CO{\cdot}O{\cdot}CO} \\ \qquad\qquad\quad | \qquad\quad | \\ \mathrm{CO_2H{\cdot}CH_2{\cdot}C{=\!=\!=}C{\cdot}C_{16}H_{33}}, \end{array}$$

whilst at 155—160° it loses carbon dioxide and forms the *anhydride*,



$$\begin{array}{l} \mathrm{CO{\cdot}O{\cdot}CO} \\ | \qquad\quad | \\ \mathrm{CMe{=}C{\cdot}C_{16}H_{33}}, \end{array}$$

which separates from aqueous methyl alcohol in colourless crystals, m. p. 35—36°, does not react with bromine in chloroform solution, but decolorises potassium permanganate in cold aqueous alcoholic sodium carbonate solution. It is concluded that agaricic acid has the structure :



$$\begin{array}{lccc} & \mathrm{CO_2H} & \mathrm{CO_2H} & \mathrm{CO_2H} \\ & | & | & | \\ \mathrm{C_{16}H_{33}}{\cdot} & \mathrm{C}\text{———} & \mathrm{C}\text{———} & \mathrm{CH_2}\,. \\ & | & | & \\ & \mathrm{H} & \mathrm{OH} & \end{array}$$

G. Y.

Dissociation Processes in the Sugar Group. I. Behaviour of Carbohydrates toward's Fehling's Solution and other Oxidising Agents. John U. Nef (*Annalen*, 1907, 357, 214—312. Compare Abstr., 1905, i, 3).—The product of the action of Fehling's solution and of aqueous copper acetate on dextrose and lævulose, considered previously to consist chiefly of *d*-*αβγ*-trihydroxy-*n*-butyric acid, has been found to be a mixture of monobasic hydroxy-acids which have now been separated and identified. Similarly, mixtures of products are formed by the action of aqueous sodium hydroxide on formaldehyde and on the di-, tri-, tetr-, pent-, and hex-oses. The amounts of the various products formed were determined quantitatively in all the cases.

1. *Products of the Oxidation of Arabinose by means of Copper Hydroxide and Sodium Hydroxide.*—If sodium hydroxide and sufficient of the hexose to reduce the copper completely are added to an aqueous solution of copper sulphate and the mixture heated, the oxidation of dextrose or lævulose commences at 40°, but that of *d*-mannose not below 92°, whilst *l*-arabinose occupies an intermediate position. Contrary therefore to the usual view, *d*-mannose, dextrose, and lævulose cannot be in complete equilibrium in alkaline solution, since if they were they must undergo oxidation under the same conditions and yield the same products. The amount of the hexose required for complete reduction of the copper and the proportions in which the products are formed varies with the amount of sodium hydroxide added.

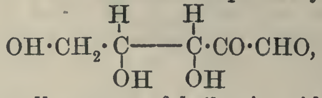
Oxidation of *l*-arabinose with copper hydroxide in alkaline solution leads to the formation of carbon dioxide, formic acid, and a number of non-volatile acids, which after acidification and evaporation of the oxidation filtrate are extracted partly by ether and partly by ethyl acetate. The ethereal extract yields *l*-glycollic acid and traces of oxalic acid, which are separated as the calcium salts, *l*-ribonic acid, which is isolated as the phenylhydrazide, and a residue containing glycollic, glyceric, *dl*-erythronic, and *dl*-threonic acids. The ethyl acetate extract yields *l*-arabonic acid and small amounts of *l*-ribonic acid.

Glycollic acid is identified by formation of its *phenylhydrazine* salt, which crystallises slowly, but almost completely, from alcohol in hexagonal plates, m. p. 100—101°, and decomposes slowly at the ordinary temperature, quickly at 100°, evolving gas.

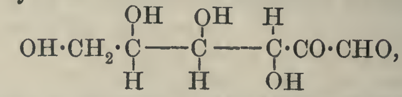
As arabonic and ribonic acids occur, not only amongst the oxidation products of *l*-arabinose, but also together with *d*-gluconic and mannonic acids in the oxidation products of dextrose, lævulose, and mannose, their salts were studied with the object of finding methods of separation. *l*-Arabonic acid forms sparingly soluble, crystalline salts with *brucine*, decomp. 155°, *quinine*, m. p. 164°, and *strychnine*, decomp. 125—130°, and a sparingly soluble, resinous salt with *morphine*. *Brucine* d-*gluconate*, decomp. 120—125° when dried in air, 150—155° when dried over sulphuric acid in a vacuum. *d*-Gluconic and *l*-arabonic acids are separated by means of the *cinchonine* salts; the *d*-gluconate crystallises almost completely from alcohol, whilst the *l*-arabonate forms a readily soluble gum. The calcium salts are less satisfactory as a means of separation, since their solubilities are often modified to a marked extent by the presence of other hydroxy-acids.

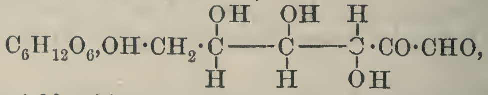
l-Ribonic acid forms a crystalline lactone, phenylhydrazide, and cadmium salt; the brucine, cinchonine, and strychnine salts are readily soluble in alcohol. *l*-Arabonic and *l*-ribonic acids are separated best by conversion into the phenylhydrazides; on digestion with absolute alcohol, *l*-arabonylphenylhydrazide remains undissolved, whilst *l*-ribonylphenylhydrazide crystallises from the filtrate on concentration. These hydrazides are hydrolysed by dilute alkalis at 100°; isomerisation of the hydroxy-acid does not take place during the hydrolysis.

As the intermediate product in the formation of $\alpha\beta\gamma\delta$-tetrahydroxyvaleric acids from *l*-arabinose is probably the pentosone,



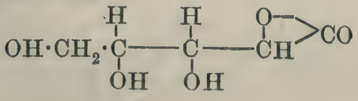
$$OH\cdot CH_2\cdot\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}\cdot CO\cdot CHO,$$

the comparatively small amount of *l*-ribonic acid formed is remarkable. The hexosone,  $OH\cdot CH_2\cdot\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}\cdot CO\cdot CHO$, formed from *d*-mannose, dextrose, or lævulose, yields *d*-gluconic acid with only traces of *d*-mannonic acid, whilst the osone,

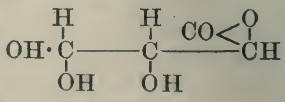


$$C_6H_{12}O_6,OH\cdot CH_2\cdot\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}\cdot CO\cdot CHO,$$

from maltose, yields chiefly glucosido-*d*-mannonic acid. It is argued from the point of view of the author's dissociation hypothesis that the pentosone from *l*-arabinose must undergo an unsymmetrical "benzilic acid transformation" forming (I), from which *l*-arabonic acid is derived together with only small amounts of (II), which yields *l*-ribonic acid.



(I.)



(II.)

Similar arguments are employed to explain the formation of optically active lactic acid by the action of enzymes on hexoses, and of *l*-alanine from *l*-bromopropionic acid (Fischer, Abstr., 1907, i, 192).

Glycollic, glyceric, *dl*-erythronic, and *dl*-threonic acids are formed probably, not only by oxidation of *l*-arabinose, but also from all aldo- and keto-pentoses and -hexoses. These acids are separated by conversion into a mixture of strychnine glycollate and *dl*-erythronate, m. p. 125—160°, and a mixture of brucine *l*-threonate, *dl*-glycerate, and *dl*-erythronate, m. p. 190—207°, the *d*-threonic acid remaining in the alcoholic filtrate. When heated with acetic anhydride, glycollic acid forms *acetylglycollic acid,* which crystallises in needles, m. p. 68—70°, and is readily soluble in water, whereas *dl*-erythronic acid forms an oily *acetyl* derivative, insoluble in water. This difference is utilised to separate the acids from the mixture of strychnine salts. The acids from the mixture of brucine salts are separated in the same manner. The soluble acetylated oil on hydrolysis yields *dl*-glyceric acid, forming an optically active calcium salt, m. p. 135°; the insoluble oil on hydrolysis yields a mixture of *dl*-erythronic and *l*-threonic acids, which are separated by means of their brucine salts. *Brucine* l-*threonate*, needles, m. p. 200°, sparingly soluble, hot alcohol. *Brucine* d-*threonate* melts at a low temperature, and is readily soluble. l-*Threonylphenylhydrazide,* flat needles, m. p. 158°, $[\alpha]_D^{20}$ $-26{\cdot}88°$, on hydrolysis with 10% potassium hydroxide yields l-*threonic acid* as a lævorotatory syrup.

It is shown that when heated with hydrochloric acid at 100°, and thereafter treated as in the separation of the oxidation products of *l*-arabinose, *dl*-erythronic acid remains unchanged, and that the same products of oxidation are obtained when carbohydrates are heated with alkalis and a limited amount of mercuric oxide in place of copper hydroxide, from which it is concluded that the four trihydroxybutyric acids are formed directly from pentoses or hexoses, and not through intermediate formation of aldotetroses.

dl-Erythrolactone (m. p. 89—90°: Ruff, Abstr., 1901, i, 449; 91°: Lespieau, Abstr., 1905, i, 566), formed by treating the calcium salt with oxalic acid, crystallises in monoclinic prisms [$a:b = 1{\cdot}6509$: about 1; $\beta = 86°35'$], m. p. 92—95°, b. p. 195—200°/14 mm. (slight decomp.). dl-*Erythronylphenylhydrazide,* $C_{10}H_{14}O_4N_4$, formed by the action of phenylhydrazine on the lactone, crystallises in white plates, m. p. 150—151°. *Dibenzoyl*-dl-*erythrolactone,* $C_{18}H_{14}O_6$, forms transparent crystals, m. p. 118°.

The mechanism of the reactions by which the products of the oxidation of 1-arabinose by copper hydroxide in alkaline solution are formed is discussed.

2. *Products of the Oxidation of* d-*Mannose, Dextrose, and Lævulose by Copper Hydroxide and Sodium Hydroxide.*—The oxidation of *d*-mannose, dextrose, and lævulose leads to the formation of the same products as are obtained from *l*-arabinose with the exception that *d*-gluconic acid and smaller amounts of *d*-mannonic acid are obtained in place of *l*-arabonic and *l*-ribonic acids. Moreover, *dl*-glyceric acid is formed in larger, glycollic acid in smaller, amounts than from the pentose. As *d*-gluconic and *d*-mannonic acids form insoluble hydrazides

with phenylhydrazine in cold alcoholic solution, the non-volatile acids formed from the hexoses are separated in the same manner as those from *l*-arabinose.

When heated with hydriodic acid, D 1·96, at 100°, glyceric acid yields *β*-iodopropionic acid; as glycollic, lactic, and erythronic acids do not undergo this reaction, it is utilised in the determination of the glyceric acid present in mixtures.

On digestion with cinchonine in aqueous solution, gluconic acid is partly transformed into a *polymeric anhydride,* which is obtained as a viscid oil, is very sparingly soluble in alcohol, and remains unchanged when heated with 10% sodium hydroxide or hydrochloric acid at 100°, but is gradually converted into gluconylphenylhydrazide by the action of an excess of phenylhydrazine at 100°. Calcium *d*-gluconate has $[\alpha]_D^{20} + 10{\cdot}5°$ ($+9{\cdot}9°$: Alberda van Ekenstein, Jorissen, and Reicher, Abstr., 1897, ii, 129).

3. *Behaviour of Carbohydrates in Dilute Alkali Hydroxide Solution towards Excess of Silver Oxide.*—When treated with an excess of silver oxide in aqueous alkali solution, the carbohydrates, whether di-, tri-, tetr-, pent-, or hex-oses, yield carbon dioxide, oxalic acid, and formic acid, only the proportions varying with the individual carbohydrate and probably with the concentration. Ten grams of each of the following substances were oxidised with an excess of silver oxide in presence of baryta in aqueous solution; the numbers given are grams of the oxidation products in the order: carbon dioxide, oxalic acid, formic acid.

Dextrose, 2·256, 8·534, 3·845; lævulose, 2·6, 8·273, 3·53; *d*-galactose, 2·995, 6·447, 4·3625; *l*-arabinose, 2·934, 8·02, 3·7294; erythritol, 2·256, 8·92, 3·427; glycerol, 5·056, 3·372, 4·8852; glycolylaldehyde, formed by heating trihydroxybutyric acid at 56—60°, 5·336, 5·362, 2·622; ethylene glycol, 4·324, 3·308, 3·1202; glycollic acid, 3·26, 6·094, 1·11228.

As erythritol is oxidised only when the mixture is gently heated, the carbon dioxide might be formed by oxidation of formic acid, but it is found that the formation of carbon dioxide from formic acid when treated with silver oxide and baryta commences and that only slowly at 110°. Ethylene glycol is oxidised completely only at 110°. The experiment with glycollic acid shows this to be a possible intermediate product in the oxidation of the carbohydrates.

4. *The Action of Alkali Hydroxides on Carbohydrates.*—The transformation of the aldohexoses into the *β*-ketohexoses,

$$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CO{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

or *dl*-lactic acid, by the action of alkalis (compare Bruyn and Alberda van Ekenstein, Abstr., 1896, i, 116; 1898, i, 225), and the theory of the formation of the saccharinic acids are discussed.

It is shown that the amount of lactic acid formed depends, not only on the individual carbohydrate, but also on the concentration of the alkali.

The stereoisomeric parasaccharinic acids are *αω*-hydroxyethyltrihydroxybutyric acids, and must form two pairs of optical isomerides, *Brucine* dl-*parasaccharinate* crystallises in needles, m. p. 193—194°;

the corresponding acid is a viscid syrup, which forms a *phenylhydrazide*, m. p. 125°. G. Y.

Sugars. W. ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1907, 4, 743—748).—*l*-Arabinose has been prepared from the leaves of *Adonis vernalis*; *l*-xylose from the seed envelope of *Sterculia foetida*, from buckwheat bran (*Polygonum fagopyrum*), and from rushes (*Scirpus lacustris*). Ribonic acid and arabonic acid were separated by fractional crystallisation of their phenylhydrazides, and pure ribonolactone obtained (m. p. 80°). From *d*-lyxose were prepared methyl-lyxoside, m. p. 80°, a_D + 40·2°, and benzyl-lyxoside, m. p. 44°, a_D + 80·5°.

Calcium amalgam is no better than sodium amalgam for the reduction of sugars. *p*-Nitrophenylhydrazine can be employed in the identification of sugars from glucosides. A. J. W.

Nature of Iodide of Starch. M. KATAYAMA (*Zeitsch. anorg. Chem.*, 1907, 56, 209—217. Compare Mylius, Abstr., 1887, 568; Padoa and Savari, Abstr., 1905, 1, 416).—The influence of the concentration of starch, iodine, and potassium iodide on the formation of iodide of starch has been investigated by bringing the components together in varying proportions and determining the quantity of iodide of starch produced by means of colorimetric measurements, the assumption being made that the depth of the colour is proportional to the concentration of the compound.

It is shown that, in dilute solution, the starch iodide concentration is proportional to the concentrations of iodine and starch respectively, but varies in a somewhat complicated manner with the iodide concentration. In very dilute solution, it is proportional to the second or third power of the iodide concentration, but the effect is proportionately smaller as the concentration increases, and depends also on the starch concentration.

From the observations, the conclusion is drawn that iodide of starch is to be regarded as a solid solution of iodine in starch and not as a chemical compound. G. S.

Hydrocelluloses. CARL G. SCHWALBE (*Ber.*, 1907, 40, 4523—4527; *Zeitsch. angew. Chem.*, 1907, 20, 2166—2172. Compare Abstr., 1907, i, 390).—The reducing power of a cellulose derivative can be determined as follows. After treatment with the Fehling's solution (*loc. cit.*) and thorough washing, the mass is extracted with dilute acetic acid and the copper estimated in the extract. The cellulose is again immersed in Fehling's solution, thoroughly washed, the blue copper-cellulose-alkali compound decomposed with acid, and a second copper estimation made. The difference between the two copper estimations gives the reducing power of the cellulose. The values have been determined for various cellulose products, including cotton-satin, mercerised cotton, viscose silk, Chardonnet silk, parchment paper, hydro- and oxy-celluloses. The hydrocelluloses give values differing from those obtained for celluloses treated with alkali.

The water of hydration in several cellulose products has been estimated by boiling the dry material with toluene; the water passes over with the first drops of the toluene, and may be absorbed by calcium chloride. The results obtained agree with the formula $2C_6H_{10}O_5,H_2O$ for mercerised cotton, and $6C_6H_{10}O_5,H_2O$ for hydrocellulose (Gladstone, Trans., 1852, 5, 7). It thus appears that alkalis have a hydrating effect, but acids both a hydrating and a hydrolysing effect.

The celluloses and their derivatives are divided into the following groups. 1. Celluloses and their hydrates, with very little reducing action and not dyed by basic colours. 2. Hydrocelluloses and their hydrates, with distinct reducing properties, but not dyed by basic colours. 3. Oxycelluloses and their hydrates, strong reducing properties and strongly dyed by basic colours. J. J. S.

Putrescine. D. Ackermann (*Zeitsch. physiol. Chem.*, 1907, **53**, 545—546).—The constitution of putrescine as tetramethylenediamine is confirmed by the fact that when the hydrochloride is distilled it yields pyrrolidine chloride and ammonium chloride. J. J. S.

Chemistry of Putrefaction. D. Ackermann (*Zeitsch. physiol. Chem.*, 1907, **54**, 1—31).—From the products of prolonged putrefaction of ox pancreas, the fraction of bases which are precipitated by alcoholic mercuric chloride solution, but not by alcoholic picric acid solution, yielded, besides pentamethylenediamine, three new bases, which were isolated as aurichlorides.

Marcitine, $C_8H_{19}N_3$, yields an *aurichloride*, $C_8H_{19}N_3,2HAuCl_4$, m. p. 175—178°. *Putrine*, $C_{11}H_{26}O_3N_2$, gives an *aurichloride*, $C_{11}H_{26}O_3N_2,2HAuCl_4$, forming orange-coloured, anhydrous, microscopic crystals, m. p. 109—110°. *Putridine* is either an isomeride of muscarine or of betaine, or it is an isomeride of putrine. The *aurichloride*, which was not obtained quite pure, forms yellow, rhombic leaflets, containing 1 or $2H_2O$ (according to the formula adopted), and melts at 85—87°. G. B.

Bromination of Urethane. Otto Diels and Felix Ochs (*Ber.*, 1907, **40**, 4571—4575).—*Tribromoethylidenediurethane*,

$$CBr_3\cdot CH(NH\cdot CO_2Et)_2,$$

m. p. 166—167°, obtained by heating urethane with bromine and iron, is decomposed by dilute hydrochloric acid at 160°, yielding glyoxylic acid, carbon dioxide, ethyl chloride and bromide, and ammonium bromide. Nitric acid, D 1·4, decomposes the substance, forming ethyl nitrate and bromal. The constitution of tribromoethylidenediurethane is determined also by its formation from bromal and urethane at 95° in the presence of a few drops of concentrated sulphuric acid.

Dibromourethane, $NBr_2\cdot CO_2Et$, b. p. 100—104°/10—11 mm., is obtained in a slightly impure condition as a heavy, transparent, reddish-brown oil by decomposing Hantzsch's compound,

$$4NBr_2\cdot CO_2Et,KBr$$

(Abstr., 1894, i, 363), with dilute sulphuric acid at 0°. C. S.

Thiocarbamide. Hermann Grossmann (*Chem. Zeit.*, 1907, **31**, 1195—1196).—The addition of thiocarbamide to solutions of tartaric acid, dextrose, raffinose, cane-sugar, and mannitol has practically no effect on their optical rotatory power, showing that thiocarbamide does not exist as a base in aqueous solutions.

It is shown that the sulphur in thiocarbamide and similar compounds may be readily estimated by treating the substance in an open vessel with concentrated nitric acid together with a little hydrochloric acid, and precipitating as barium sulphate. W. H. G.

Action of Dry Ammonia on Ethyl Oxalate. Isaac K. Phelps, L. H. Weed, and C. R. Housum (*Amer. J. Sci.*, 1907, [iv], 24, 479—482).—It has been stated by Liebig (*Annalen*, 1834, 9, 129) that dry ammonia acts with difficulty on ethyl oxalate to form ethyl oxamate and oxamide, the greater part of the ethyl oxalate being unaffected.

Experiments are now described which show that when cold anhydrous ethyl oxalate is treated with excess of dry ammonia, a mixture of ethyl oxamate and oxamide is produced, only a small quantity of the oxalate remaining unchanged. If contact between the reagents is facilitated by means of a medium, such as alcohol or light petroleum, the final product consists entirely of oxamide.

E. G.

Compounds of Quadrivalent Molybdenum. Julius Sand and Johanna Maas (*Ber.*, 1907, 40, 4504—4513).—Sand and Burger obtained a series of salts in which molybdenum was considered to function as a quadrivalent element by electrolytic reduction of ammonium molybdate in presence of ammonium thiocyanate (Abstr., 1906, i, 487). The present paper contains the results of a further investigation of the zinc salt, $[Mo(SCN)_6(NH_3)_4]Zn$, described by these authors.

The action of boiling acetic acid on the zinc salt leads to the formation of a yellow, crystalline *acetate*,

$$[Mo(SCN)_6(NH_3)_3(H_2O)]H_2,C_2H_4O_2,$$

in which two of the ammonia groups are co-ordinated, on the one hand, with molybdenum and, on the other, with hydrogen. The curve representing the molecular conductivity of the acetate rises rapidly with increasing dilution, and closely resembles the corresponding curve for hydrofluosilicic acid. The acetate dissolves in concentrated aqueous ammonium thiocyanate, and is extracted from this by ether, forming a yellow solution which is stable if the ether has been previously dried over sodium, but otherwise becomes dark green, and finally black on exposure to air.

On reduction of a solution of ammonium molybdate and thiocyanate in hydrochloric acid with a current not exceeding two amperes and cooling the resulting solution, the *compound*,

$$[Mo(SCN)_6(NH_3)_3(H_2O)]H_2,3H_2O,$$

separates in yellow needles, which lose water and become dark over sulphuric acid in a vacuum. If the crude product from the electrolytic reduction is dissolved in absolute alcohol, addition of benzene precipitates a *compound*, $[Mo(SCN)_6(NH_3)_3(H_2O)]H_2,\frac{1}{2}C_2H_6O,2H_2O$, or $[Mo(SCN)_6(NH_3)_3(H_2O)]H_2,\frac{2}{3}C_2H_6O,H_2O$. Similarly, recrystallisation of the crude reduction product from propyl alcohol leads to the formation of the *compound*, $[Mo(SCN)_6(NH_3)_3(H_2O)]H_2,\frac{2}{3}C_3H_8O,H_2O,\frac{1}{3}HCl$. When treated with acetic acid, the three preceding compounds yield the acetate obtained from the zinc salt, or, with propionic acid, the *propionate*, $[Mo(SCN)_6(NH_3)_3(H_2O)]H_2,\frac{2}{3}C_3H_6O_2,H_2O$.

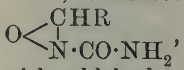
When boiled with alcoholic ethylenediamine, the compound containing $\frac{1}{2}$ or $\frac{2}{3}C_2H_6O$ yields the complex *substance*,

$$\{Mo(SCN)_6[C_2H_4(NH_2)_2]_3(H_2O)\}H_2,2C_2H_4(NH_2)_2,$$

which forms yellow crystals, m. p. 106—107°, gives with ammonia a *derivative* containing both ammonia and ethylenediamine, forms a yellow *zinc* salt with aqueous zinc chloride, and is converted by acids into *thiocyanates* containing smaller proportions of the diamine.

The quadrivalency of the molybdenum atom in the yellow series of thiocyanates is confirmed by heating Sand and Burger's zinc salt with concentrated hydrochloric acid in a current of carbon dioxide, when thiocyanic acid is slowly evolved and the product on addition of manganese sulphate and dilute sulphuric acid and titration with potassium permanganate gives results agreeing with those calculated for the conversion of quadrivalent into sexivalent molybdenum.

G. Y.

Hydroxycarbamides and Carbamidoximes. I. A. CONDUCHÉ (*Ann. Chim. Phys.*, 1907, [viii], **12**, 533—574).—Mainly a detailed account of work already published (Abstr., 1905, i, 289 ; 1906, i, 593). In view of the fact that *iso*hydroxycarbamide, m. p. 70—72°, condenses with aldehydes to form carbamidoximes of the type  $O<\begin{array}{l}CHR\\ |\\ N\cdot CO\cdot NH_2\end{array}$, whilst the isomeride, m. p. 140°, does not react with aldehydes, the author suggests that *iso*hydroxycarbamide has the constitution: $OH\cdot NH\cdot CO\cdot NH_2$, that of its isomeride being represented by the formula $OH\cdot C(NH_2){:}N\cdot OH$ (compare Francesconi and Parrozzani, Abstr., 1902, i, 139).

M. A. W.

Action of Semicarbazide on Unsaturated Compounds. II. HANS RUPE and E. HINTERLACH (*Ber.*, 1907, **40**, 4764—4770. Compare Rupe and Lotz, Abstr., 1903, i, 841 ; Rupe and Schlochoff, Abstr., 1904, i, 144).—The addition of hydroxylamine to compounds is not so much affected by constitutional influences as is the addition of semicarbazide. It was not found possible to add on semicarbazide to a cyclic, unsaturated ketone. The action of semicarbazide on ethylideneacetone, *iso*valerylideneacetone, and heptylideneacetone respectively is described. The semicarbazide-semicarbazones of these compounds are unstable; when boiled with alcohol, or with water, they are decomposed, either into their components, or the unsaturated ketones undergo further decomposition, whilst the hydrazodicarbonamide, $NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, of Thiele is produced. Ethyl ethylideneacetoacetate combines with semicarbazide to form the semicarbazide-semicarbazone in very small yield. Ethyl crotonate combines comparatively readily with semicarbazide.

Ethylideneacetonesemicarbazide-semicarbazone,
$NH_2\cdot NH\cdot CO\cdot NH\cdot CHMe\cdot CH_2\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2$,
obtained from ethylidene acetone and semicarbazide, crystallises from alcohol in needles, m. p. 126°.

*iso*Valerylideneacetone, $CHMe_2\cdot CH_2\cdot CH{:}CH\cdot COMe$, obtained from *iso*valeraldehyde and acetone, is a yellow oil with b. p. 72—73°/12 mm., whilst Barbier and Bouveault give 180°/750 mm. Its *semicarbazide-semicarbazone*,
$NH_2\cdot NH\cdot CO\cdot NH\cdot CH(CH_2\cdot CHMe_2)\cdot CH_2\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2$,
crystallises from alcohol in rhombic leaflets, m. p. 157°.

Heptylideneacetone, $CH_3\cdot[CH_2]_5\cdot CH{:}CH\cdot COMe$, obtained from heptaldehyde and acetone, boils at 125—126°/12 mm., and forms needles, m. p. 16—17°. Its *semicarbazide-semicarbazone*,
$CH_3\cdot[CH_2]_5\cdot CH(NH\cdot CO\cdot NH\cdot NH_2)\cdot CH_2\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2$,
crystallises from alcohol in tiny needles, m. p. 156—157°.

Ethyl ethylideneacetoacetate semicarbazide-semicarbazone,
$CMe({:}N\cdot NH\cdot CO\cdot NH_2)\cdot CH(CO_2Et)\cdot CHMe\cdot NH\cdot NH\cdot CO\cdot NH_2$,
forms leaflets, m. p. 168°.

The *compound*, $NH_2\cdot NH\cdot CO\cdot NH\cdot CHMe\cdot CH_2\cdot CO_2Et$, obtained from ethyl crotonate and semicarbazide, crystallises from alcohol in cubes, m. p. 127°. The main product of the action is, however, the *compound*, $NH_2\cdot NH\cdot CO\cdot NH\cdot CHMe\cdot CH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, which crystallises from alcohol in tiny, stellate needles, m. p. 151°.

A. McK.

Action of Amorphous Arsenic on Alkyl-halide Derivatives. VICTOR AUGER (*Compt. rend.*, 1907, **145**, 808—811).—The amorphous arsenic, obtained by reducing a hydrochloric acid solution of arsenious oxide with stannous chloride or sodium hypophosphite, is of very great chemical activity. When heated in a sealed tube at 160° with carbon tetrachloride, arsenic trichloride and carbon tetrachloride are formed; with chloroform, the products are arsenic trichloride, hydrogen chloride, and amorphous carbon, and with ethylene bromide, or iodide, ethylene and arsenic tribromide or tri-iodide. When methyl iodide is treated with amorphous arsenic at the ordinary temperature or on a water-bath, there are formed arsenic tri-iodide, tetramethylarsonium iodide, a large quantity of methylarsine iodide, $AsMeI_2$, and a trace of cacodyl iodide. Ethyl iodide reacts more slowly, giving 16% of AsI_3, 16% of $AsEt_4I$, and 60% of $AsEtI_2$. The higher aliphatic iodides also react with amorphous arsenic. At the temperature of the water bath, amorphous arsenic reacts explosively with iodoform, but in the presence of a neutral solvent (benzene or toluene) the reaction: $3MeI + 2As = CHI_2\cdot AsI_2 + As(CHI_2)_2I$ takes place quantitatively. The dense, black oil formed is oxidised by cold nitric acid according to the equations:

$$CHI_2\cdot AsI_2 + 4HNO_3 = CHI_2\cdot AsO(OH)_2 + 4NO_2 + H_2O + I_2;$$
$$As(CHI_2)_2I + 3HNO_3 = As(CHI_2)_2O\cdot OH + 3NO_2 + H_2O + I.$$

Di-iodomethylarsonic acid, $CHI_2\cdot AsO(OH)_2$, crystallises in large, yellow, efflorescent tablets containing $1H_2O$. It forms dibasic salts; that of *silver* is an insoluble, white precipitate, which is decomposed by boiling nitric acid, forming arsenic acid and liberating iodine. The acid is decomposed by hot aqueous alkali hydroxides, thus:

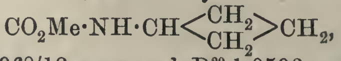
$$CHI_2\cdot AsO(OH)_2 + 2NaOH = CH_2I_2 + Na_2HAsO_4 + H_2O.$$

It is also decomposed by hydrochloric acid.

Tetraiodocacodylic acid, $As(CHI_2)_2O\cdot OH$, forms small, sulphur-yellow crystals, insoluble in water, but soluble in boiling nitric acid or much acetic acid. It is completely decomposed by prolonged boiling with the former acid. With hot alkali, the reaction is similar to that with the first acid. The *sodium* salt crystallises from 90% alcohol in large, yellow tablets containing $6H_2O$. E. H.

Convenient Method for the Preparation of *cyclo*Propane. Hugo Haehn (*Arch. Pharm.*, 1907, **245**, 518—519).—*cyclo*Propane is readily prepared by heating 16 grams of amyl alcohol and 10 grams of trimethylene bromide with 3·3 grams of zinc wool; about 650 c.c. of the compound, containing traces of propylene, are obtained by this method in an hour. W. H. G.

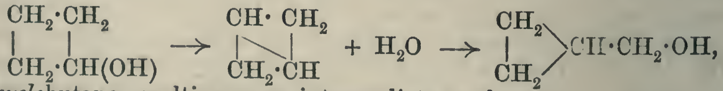
Constitution of *cyclo*Butene. Nicolai Zelinsky and Johannes Gutt (*Ber.*, 1907, **40**, 4744—4749. Compare Willstätter and Bruce, Abstr., 1907, i, 1018).—*cyclo*Butanecarboxylic acid has D_4^{11} 1·0683, not D_4^{20} 1·0538, as given by Brühl. It was converted first into its acid chloride, then into its amide, and finally into the *urethane*,



$$CO_2Me\cdot NH\cdot CH{<}{\substack{CH_2\\CH_2}}{>}CH_2,$$

m. p. 19°, b. p. 95—96°/12 mm., and D_4^{20} 1·0593; when distilled with calcium hydroxide, it forms cyclo*butylamine*, C_4H_9N, D_4^{20} 0·8328, D_4^{10} 0·8422, and n_D^{19} 1·4363.

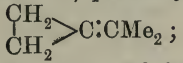
*cyclo*Butanol, obtained by the action of a slight excess of potassium nitrite on an aqueous solution of the preceding amine, has b. p. 123°/740 mm., D_4^{20} 0·9159, and n_D^{20} 1·4328. After *cyclo*butanol had been oxidised by an aqueous solution of chromic acid, the product was submitted to steam distillation, and the first 10 c.c. of the distillate saturated with potassium carbonate. The oil, obtained in this manner, coloured magenta-sulphurous acid red, and boiled at 90—110°; the semicarbazone obtained from it had m. p. 216° (decomp.), whereas *cyclo*butanonesemicarbazone has m. p. 201° according to Kijner. A partial isomerisation of *cyclo*butanol had accordingly taken place, thus:



di*cyclo*butane resulting as an intermediate product.

It is probable that, under the conditions employed by Willstätter and Bruce, di*cyclo*butane would result from the dry distillation of the product, obtained by the interaction of silver oxide and *cyclo*butylammonium iodide. All the transformations of the "*cyclo*butene" of Willstätter and Bruce could be accounted for on the basis of the dicyclic structure referred to. A. McK.

Scission of the Trimethylene Ring by Catalytic Reduction. Nicolai Zelinsky (*Ber.*, 1907, 40, 4743—4744. Compare Willstätter and Bruce, Abstr., 1907, i, 1018).—With the view of studying the behaviour of the trimethylene ring when unsaturated derivatives of *cyclo*propane are reduced by hydrogen in the presence of nickel according to Sabatier and Senderens, the author examined the reduction of dimethylmethylene*cyclo*propane. The latter hydrocarbon (Abstr., 1901, i, 660; 1902, i, 70) probably has the formula:

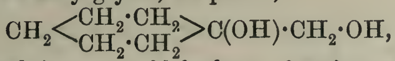


$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>C{:}CMe_2\,;$$

it has b. p. 69—69·5°/718 mm., and has n_D^{17} 1·4264. When the mixture of its vapour and hydrogen is passed over nickel at 160°, the action: $C_6H_{10} + 2H_2 = C_6H_{14}$ takes place, the trimethylene ring being disrupted. The resulting hydrocarbon has b. p. 59—59·5°/732 mm., D_4^{17} 0·6583, and n_D^{17} 1·3723. The b. p. is the same as that of *β*-methylpentane, so that the trimethylene ring appeared to be disrupted between the secondary and tertiary carbon atoms.

A. McK.

Isomeric Rearrangement. Methylene*cyclo*hexane. Alexei E. Faworsky and I. Borgmann (*Ber.*, 1907, 40, 4863—4875).—Methyl*cyclo*hexanol, prepared from phenol by a modification of Sabatier's method in which nickel is replaced by nickelised asbestos, forms a *bromide*, b. p. 163—165·5°, D_0^0 1·3604. cyclo*Hexylcarbinol*, prepared by the Grignard method, has b. p. 184—186°/784 mm., D_0^0 0·9445, and yields an *acetate*, b. p. 199—201°/740 mm. The *iodide*, $CH_2{<}\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}{>}CH{\cdot}CH_2I$, formed by the action of saturated hydriodic acid, has b. p. 102—104°/28 mm. or 213°/743 mm., and D^0 1·555. When treated with alcoholic potash by Butleroff's method, it yields *methylene*cyclo*hexane*, $CH_2{<}\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}{>}C{:}CH_2$, b. p. 102—103°/760 mm., D_0^0 0·8184, which forms an additive *dibromide*, $C_7H_{12}Br_2$, b. p. 121·5—123°/27 mm., D_0^0 1·7156; this, when hydrolysed, forms a primary tertiary glycol, m. p. 76°,



$$CH_2{<}\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}{>}C(OH){\cdot}CH_2{\cdot}OH,$$

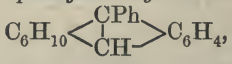
which is converted into an aldehyde on heating with 1% sulphuric acid.

*Methylene*cyclo*hexane chloronitrosite* forms colourless, plate-like crystals, m. p. 118° (heated slowly) or 145° (heated quickly) with decomposition; the *piperidide*, $C_7H_{12}ON{\cdot}C_5NH_{10}$, has m. p. 127·5—128°. Oxidation of the hydrocarbon with potassium permanganate leads to the formation of the glycol just mentioned, which has been described previously by Wallach.

Methylene*cyclo*hexane remains unaltered when heated with quinoline, but in presence of quinoline and quinoline hydriodide it is converted into methyl-Δ^1-*cyclo*hexene, b. p. 109·5—110°, which forms a *chloronitrosite*, $C_7H_{12}NOCl$, m. p. 97·5° (decomp. 115°).

The hydrocarbons described by Zelinsky and Gutt, by Sabatier, and by Wallach as methylene*cyclo*hexane are shown to have been isomerides of this compound. E. F. A.

The Hydroanthracenes and their Derivatives. Marcel Godchot (*Ann. Chim. Phys.*, 1907, [viii], 12, 468—533).—A detailed account of work already published (compare Abstr., 1904, i, 987; 1905, i, 201; 1906, i, 76, 494; 1907, i, 308, 836, 840, 841). The following facts are new: 9-benzylhexahydroanthracene (Abstr., 1907, i, 308) can also be prepared by the action of magnesium benzyl chloride on hexahydroanthrone; 9-*phenylhexahydroanthracene*,

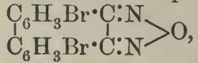


$$C_6H_{10}\Big<\begin{array}{c}CPh\\ |\\ CH\end{array}\Big>C_6H_4,$$

similarly prepared from magnesium phenyl bromide and hexahydroanthrone, is a yellow oil, b. p. 235°/15 mm., and dissolves in ether or benzene to form beautiful blue, fluorescent solutions. M. A. W.

Phenanthrene Series. XXII. 2:7-Dibromophenanthrene and 2:7-Dibromophenanthraquinone. Julius Schmidt and Robert Mezger (*Ber.*, 1907, 40, 4560—4566).—The bromination of α-tetrahydrophenanthrene (Abstr., 1907, i, 1022) in chloroform yields 2:7-*dibromophenanthrene*, $C_{14}H_8Br_2$, m. p. 199—200°, which separates from alcohol in long, colourless needles; the position of the halogen is determined by the oxidation of the compound to 2:7-dibromophenanthraquinone (Abstr., 1904, i, 1034).

2:7-*Dibromophenanthraquinone dioxime*, $C_{14}H_8O_2N_2Br_2$, m. p. 290° (decomp.), crystallises in yellow needles; the *diacetyl* derivative, $C_{18}H_{12}O_4N_2Br_2$, m. p. 250° (decomp.), forms sulphur-yellow needles, and is hydrolysed very readily. 2:7-*Dibromophenanthrafurazan*,



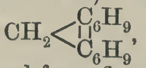
$$\begin{array}{l}C_6H_3Br\cdot C{:}N\\ \;|\qquad\qquad\;|\\ C_6H_3Br\cdot C{:}N\end{array}\Big>O,$$

m. p. 306°, is obtained from the dioxime, benzoyl chloride, and sodium hydroxide, and forms colourless needles.

With reference to the question of colour and constitution, a comparison of the preceding compounds with the corresponding compounds of phenanthraquinonedioxime (Abstr., 1907, i, 630, 1022) shows that one and the same quinonoid nucleus can yield colourless or coloured derivatives according as the nuclear carbon atoms are attached to hydrogen or to bromine.

Saturated solutions of 9-bromophenanthrene and of picric acid, mixed at the ordinary temperature, yield yellow needles of the *picrate*, $C_{14}H_9Br,C_6H_2(NO_2)_3OH$, m. p. 118°. C. S.

Hydrogenation of Fluorene. Julius Schmidt and Robert Mezger (*Ber.*, 1907, 40, 4566—4570).—*Decahydrofluorene*,

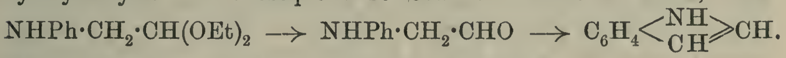


$$CH_2\Big<\begin{array}{l}C_6H_9\\ |\\ C_6H_9\end{array},$$

b. p. 258°/737 mm., is obtained from fluorene, hydriodic acid (D 1·96), and red phosphorus at 175° in an atmosphere of carbon dioxide, or from fluorene under Sabatier and Senderens' conditions at 150°. It has D_4^{20} 1·012, n_D^{20} 1·5060, gives yellow to violet colorations with warm concentrated sulphuric acid, and a dark violet coloration with potassium dichromate and concentrated sulphuric acid, changing to bluish-green by dilution.

Liebermann and Spiegel's fluorene perhydride (Abstr., 1889, 719) and Guye's compound (Abstr., 1891, 314) are shown to be the decahydride. C. S.

Anilinoacetal. ALFRED WOHL and M. LANGE (*Ber.*, 1907, 40, 4727—4730. Compare Wohl, Abstr., 1888, 443).—Anilinoacetal was prepared in the hope that it would be possible to obtain indole from it by hydrolysis and subsequent removal of 1 mol. of water, thus:



$$\mathrm{NHPh\cdot CH_2\cdot CH(OEt)_2} \longrightarrow \mathrm{NHPh\cdot CH_2\cdot CHO} \longrightarrow \mathrm{C_6H_4}{<}\genfrac{}{}{0pt}{}{\mathrm{NH}}{\mathrm{CH}}{>}\mathrm{CH}.$$

This condensation could not, however, be effected.

Anilinoacetal, $\mathrm{NHPh\cdot CH_2\cdot CH(OEt)_2}$, cannot be prepared by heating aniline and chloroacetal together, but may be obtained by adding these two substances to finely-divided sodamide suspended in ether; it is an oil, b. p. 92—94°/0·24—0·30 mm. Hydrolysis of this compound by acids does not result in the liberation of the corresponding aldehyde; instead, water splits off with the alcohol group and polymerisation ensues, the *substance*, $(\mathrm{C_8H_7N})_6$, being produced. It is a greyish-white, amorphous substance, decomposing at 248°, and does not give the pine-shaving reaction.

A mixture of alcohol, sodium ethoxide, sodium iodide, formanilide, and chloroacetal heated under pressure at 150—160° for ten hours yields the *acetal*, $\mathrm{CHO\cdot NPh\cdot CH_2\cdot CH(OEt)_2}$, but it cannot be separated from unaltered formanilide. W. H. G.

Phenyl Derivatives of Primary Aromatic Amines. IRMA GOLDBERG [and FRL. C. SISSOEFF] (*Ber.*, 1907, 40, 4541—4546. Compare Abstr., 1906, i, 426; Lambé, Abstr., 1907, i, 941).—Practically all primary arylamines are converted into corresponding diphenylamine derivatives when boiled with bromobenzene, potassium carbonate, and cuprous iodide in nitrobenzene solution for some hours. The cuprous iodide can be replaced with advantage by a mixture of potassium iodide and copper, and better yields are obtained when the acetyl derivatives of arylamines are used.

The following have been prepared by this method: acetyldiphenylamine; *acetylphenyl*-p-*tolylamine*, m. p. 52°; phenyl-*p*-tolylamine; *acetylphenyl*-m-*xylylamine* [$\mathrm{Me_2 : NAc = 1 : 3 : 4}$], m. p. 115°; *phenyl*-m-*xylylamine* [$\mathrm{Me_2 : NH = 1 : 3 : 4}$], m. p. 43°; m-*nitrodiphenylamine*, m. p. 112°; *o*-nitrodiphenylamine, m. p. 75°, and p-*nitrodiphenylamine*, m. p. 133°. J. J. S.

Coloured and Colourless Modifications of the Silver Salts of Halogen Phenols. ARTHUR HANTZSCH and KARL SCHOLTZE (*Ber.*, 1907, 40, 4875—4883. Compare Torrey and Hunter, this vol., i, 1030).—Salts of phenols which do not contain halogen are colourless and easily decompose; as halogen is introduced their stability is increased, and the salts of the tri-, tetra- and penta-halogen phenols are almost as stable as silver acetate. Coloured salts, varying from yellow to orange-red, exist of some of these, which sometimes contain water, but in other cases are anhydrous, and have then the same composition as the colourless salts. The coloured silver salts are the primary form, as they result at once when the alkali salts are precipitated by silver nitrate; the colourless salts are quite stable, but they can to some extent be converted into the coloured salts by carefully acidifying their solutions in pyridine or ammonia. The coloured salts are most readily transformed into the colourless forms in presence of a moist solvent, but they are quite stable when completely dry.

The *silver* salts of *o*-, *m*-, and *p*-chlorophenol are colourless and decompose very rapidly; that of 2 : 4-*dichlorophenol* behaves similarly. *Silver dichloro*-p-*cresol*, m. p. 39°, is of a deep yellow colour, which becomes green as decomposition takes place. *Silver*-2 : 4 : 6-*trichlorophenol* is more stable, and cannot be converted into a colourless salt; the yellow compound crystallises with a molecule of water. *Silver tetra*- and *penta-chlorophenol* are yellow and orange respectively; the latter is not convertible into a colourless modification.

The *silver* salts of p-*bromo*- and 2 : 4-*dibromo-phenol* are colourless. *Silver*-2 : 6-*dibromo*-p-*cresol* forms a primary, labile, orange-coloured salt, $C_6H_2MeBr_2OAg,3H_2O$, decomposing at 135°, which, when moist, very rapidly goes over into the stable, colourless salt. Silver-2 : 4 : 6-tribromophenol was obtained in orange-red and colourless modifications (compare Torrey and Hunter, *loc. cit.*). The coloured salt only slowly changes into the colourless form; both modifications form an ammoniate, $C_6H_2Br_3OAg,2NH_3$. The *silver* salts of tetra- and penta-bromophenol and of tetrabromo-*p*-cresol are colourless.

The *silver* salts of *p*-iodo- and 2 : 4-di-iodo-phenol are colourless, as also are those of 2:6-di-iodo-*p*-cresol and 2:4:6-tri-iodophenol. E. F. A.

Position of the Iodine in the Two Known Iodoguaiacols. EFISIO MAMELI (*Gazzetta*, 1907, **37**, ii, 366—379).—The structure of the 4-iodoguaiacol, m. p. 43°, prepared by Mameli and Pinna (*Arch. Farm. sper. Sci. affini*, 1907, **6**, 193) by reducing benzeneazoguaiacol, diazotising the 4-aminoguaiacol, and decomposing the diazo-salt in presence of cuprous iodide, is confirmed. The compound, described by Tassilly and Leroide (Abstr., 1907, i, 515) as 4-iodoguaiacol, is really 5-iodoguaiacol, its constitution having been based on that of Cousin's 4-nitroguaiacol (*J. Pharm. Chim.*, 1899, [vi], **9**, 276), which Paul (Abstr., 1906, i, 843) has shown to be 5-nitroguaiacol.

The positions of the iodine in these two iodoguaiacols have been further verified as follows. Cousin's nitroguaiacol (*loc. cit.*) was reduced to aminoguaiacol, which was diazotised and the diazo-derivative decomposed with cuprous cyanide; hydrolysis of the resulting 5-cyanoguaiacol (*vide infra*) yielded the corresponding known acid, *iso*vanillic acid. Similar treatment of the aminoguaiacol from which the author and Pinna (*loc. cit.*) prepared their iodoguaiacol resulted in the formation of vanillic acid.

5-*Cyanoguaiacol* or iso*vanillonitrile*,

$$OH\cdot C_6H_3(OMe)CN\ [OH : OMe : CN = 1 : 2 : 5],$$

crystallises from water in shining, brick-red needles, m. p. 124°, dissolves readily in ether and sparingly in alcohol or benzene, and gives a violet coloration with ferric chloride. T. H. P.

Iodohydrins and Alkyliodohydrins derived from Styrene. Marc Tiffeneau (*Compt. rend.*, 1907, **145**, 811—813).—By the action of iodine and yellow mercuric oxide on styrene in the presence of ether, phenylethylene iodohydrin, $\mathrm{OH\cdot CHPh\cdot CHPh\cdot CHI}$, is alone formed, but in the presence of an alcoholic solvent an alkyl iodohydrin, $\mathrm{OR\cdot CHPh\cdot CH_2I}$, is also produced. In all cases, the hydroxyl combines with the carbon atom nearer to, the iodine with that farther from, the aromatic group (compare Abstr., 1906, i, 965). The constitution of the alkyliodohydrins is proved by their transformation by alcoholic potash into α-alkyloxystyrenes: $\mathrm{OR\cdot CHPh\cdot CH_2I \longrightarrow OR\cdot CPh{:}CH}$. Phenylethylene iodohydrin (compare Abstr., 1907, i, 404) has b. p. 148—152°/18 mm., and D^0 1·667; it soon decomposes, forming acetophenone.

When heated with sodium methoxide, *phenylethylene ω-methyl ether*, $\mathrm{OH\cdot CHPh\cdot CH_2\cdot OMe}$, b. p. 132°/18 mm., 237—238°/760 mm., D^0 1·080, and a *compound*, $\mathrm{C_{16}H_{16}O_2}$, b. p. 195—197°/18 mm., D^0 1·098, which combines with bromine and easily decomposes into acetophenone, are formed. With alcoholic potash, the iodohydrin gives the *ω-ethyl ether*, b. p. 242—243°/760 mm., D^0 1·054, and a *substance*, b. p. 187—190°/15 mm. *Phenylethylene methyliodohydrin*, $\mathrm{OMe\cdot CHPh\cdot CH_2I}$, b. p. 135—138°(corr.)/14 mm., is transformed by alcoholic potash into *α-methoxystyrene*, b. p. 196—197° (corr.), D^0 1·0178, and by silver nitrate or acetate into phenylacetaldehyde, probably by the intermediate formation of ω-methoxystyrene, thus:

$$\mathrm{OMe\cdot CHPh\cdot CH_2I \longrightarrow OMe\cdot CH{:}CHPh \longrightarrow CHO\cdot CH_2Ph.}$$

Phenylethylene ethyliodohydrin, $\mathrm{OEt\cdot CHPh\cdot CH_2I}$, b. p. 142—144°/16 mm., D^0 1·530, is converted by alcoholic potash into *α-ethoxystyrene*, b. p. 209—210° (corr.), D^0 0·991. *Phenylethylene amyliodohydrin*, $\mathrm{OC_5H_{11}\cdot CHPh\cdot CH_2I}$, b. p. 170—175°/15 mm., is transformed by alcoholic potash into *α-amyloxystyrene*, b. p. 255—259°, D^0 0·943, and by silver nitrate into phenylacetaldehyde and amyl alcohol.

E. H.

Presence of *p*-Methoxycinnamaldehyde in Essential Oil of Tarragon, and some Derivatives of Estragole. Maurice Daufresne (*Compt. rend.*, 1907, **145**, 875—877).—Essential oil of tarragon contains from 4·5% to 0·5% of *p*-methoxycinnamaldehyde, which is isolated from the higher boiling fractions as a yellow oil, b. p. 171°/15 mm., D 1·137, and forms an *oxime*, m. p. 154°, and a semicarbazone, m. p. 220°. Contrary to the experience of Scholtz and Wiedemann (Abstr., 1903, i, 437), the author finds that the synthetical compound prepared by the condensation of anisaldehyde with acetaldehyde has the same physical constants.

The iodohydrin of estragole yields (1) estragole oxide on treatment with powdered potassium hydroxide (compare Fourneau and Tiffeneau, Abstr., 1905, i, 591; 1906, i, 20); (2) *γ-p-methoxyphenylpropane-αβ-diol*, $\mathrm{OMe\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot CH_2OH}$, on treatment with 15% solution of aqueous potassium hydroxide, this compound has b. p. 200—205°/20 mm. and m. p. 52°; (3) the *amino-alcohol*,

$$\mathrm{OMe\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NMe_2,}$$

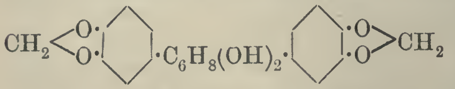
by reaction with dimethylamine, this alcohol has b. p.

166—167°/12 mm., D^0 1·038, and the hydrochloride of the *benzoyl* derivative has m. p. 98°; the corresponding *diethylamino*-compound, $OMe\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NEt_2$, has b. p. 187—189°/15 mm. or 308—310°/755 mm., D^0 0·946, and does not yield a crystalline benzoyl derivative.

The *methyliodohydrin* of estragole, $OMe\cdot C_6H_4\cdot CH_2\cdot CH(OMe)\cdot CH_2I$, b. p. 178—180°/14 mm., D^0 1·459, yields the *methyl ether* of the corresponding vinyl alcohol, $OMe\cdot C_6H_4\cdot CH_2\cdot C(OMe)\colon CH_2$, by the action of boiling potassium hydroxide solution; this compound has b. p. 144—145°/15 mm. or 262—264°(corr.)/760 mm., D^0 1·073, and is hydrolysed by dilute sulphuric acid, forming anisylacetone.

M. A. W.

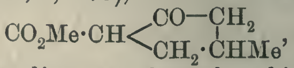
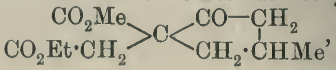
Cubebin. I. EFISIO MAMELI (*Gazzetta*, 1907, **37**, ii, 483—506).—Previous work on cubebin is first discussed. From ten samples of cubebin of different ages and origins, the author succeeded, by various methods of purification, in preparing products exhibiting the same physical properties, and thus establishing the individuality of cubebin. Pure cubebin has m. p. 132°, $[\alpha]_D^{25}$ $-45·45°$ in chloroform or benzene, and empirical formula $C_{10}H_{10}O_3$. The mean molecular weight in freezing acetic acid is 265·71, and in boiling alcohol 329·07, the formula being hence $C_{20}H_{20}O_6$. From the known chemical reactions of cubebin, it is assumed to have the annexed formula.

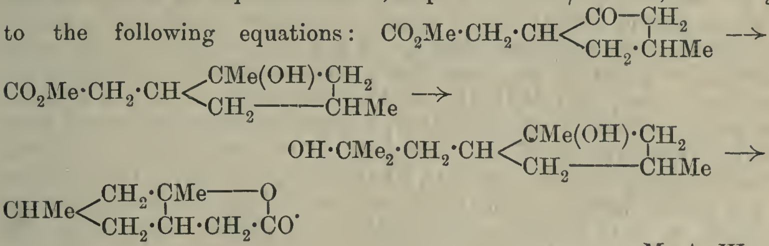


T. H. P.

Salicylic Ester of Cholesterol. L. GOLODETZ (*Chem. Zeit.*, 1907, 31, 1215).—*Cholesteryl salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot C_{26}H_{43}$, prepared in a 60% yield by heating salicylic acid with cholesterol at 160—170°, separates from a mixture of ether and alcohol in white crystals, m. p. 173°, and is hydrolysed by boiling alcoholic potassium hydroxide, forming cholesterol and salicylic acid.

G. Y.

Synthesis of β-Campholenolactone; the Lactone of 2:4-Dimethyl*cyclo*pentane-2-olacetic Acid. GUSTAVE BLANC (*Compt. rend.*, 1907, **145**, 930—932).—Preliminary to attempting the synthesis of β-campholenolactone from *αα*-dimethyladipic acid, the author has synthesised the similarly constituted compound, the lactone of 2:4-dimethyl*cyclo*pentane-2-olacetic acid, from methyl-β-methyladipate by means of the following series of reactions. Methyl β-methyladipate, when treated with sodium, yields a compound which, according to Dieckmann (Abstr., 1894, i, 173), should be *methyl methyl*cyclo*pentane-4-one-3-carboxylate*,  $CO_2Me\cdot CH<\begin{matrix}CO-CH_2\\ CH_2\cdot CHMe\end{matrix}$, but the possibility of the methyl group being adjacent to the carbonyl is not precluded. The sodium derivative of this ester reacts with ethyl bromoacetate to form the *compound*,  $\begin{matrix}CO_2Me\\ CO_2Et\cdot CH_2\end{matrix}>C<\begin{matrix}CO-CH_2\\ CH_2\cdot CHMe\end{matrix}$, a colourless liquid, b. p. 165—168°/10 mm., which, on hydrolysis, yields *methyl*cyclo*pentane-4-one-3-acetic acid*, a viscous liquid, b. p. 195°/25 mm., forming a *semicarbazone*, m. p. 205°. The *methyl* ester of this acid is a sweet smelling, mobile liquid, b. p. 128°/14 mm., forms a *semicarbazone*, m. p. 190°, and by the action of magnesium methyl iodide yields a non-crystalline *glycol*, which is converted by the action of alkalis into the required *lactone*, b. p. 127—130°/13 mm., according to the following equations:



$$CO_2Me\cdot CH_2\cdot CH{<}\begin{matrix}CO-CH_2\\ CH_2\cdot CHMe\end{matrix} \longrightarrow CO_2Me\cdot CH_2\cdot CH{<}\begin{matrix}CMe(OH)\cdot CH_2\\ CH_2\text{———}CHMe\end{matrix} \longrightarrow OH\cdot CMe_2\cdot CH_2\cdot CH{<}\begin{matrix}CMe(OH)\cdot CH_2\\ CH_2\text{———}CHMe\end{matrix} \longrightarrow CHMe{<}\begin{matrix}CH_2\cdot CMe\text{——}O\\ CH_2\cdot CH\cdot CH_2\cdot CO\end{matrix}.$$

M. A. W.

Unsaturated Compounds. V. Addition of Mercaptans to Unsaturated Acids.

THEODOR POSNER [with ROBERT BAUMGARTH] (*Ber.*, 1907, 40, 4788—4794. Compare Abstr., 1904, i, 160; 1905, i, 279; 1906, i, 955; 1907, i, 55, 212).—Previous work has shown that addition of mercaptan to an unsaturated ketone occurs at the ethylenic linking. Unsaturated hydrocarbons show, in general, the same behaviour, but there are exceptions, notably stilbene and diphenylbutadiene, and, of the fifteen diolefines examined, in thirteen cases addition only occurred at one double bond. The work has been extended to unsaturated acids of the acrylic series. In all cases, the resulting sulphide produced by the interaction of the acids and mercaptans was not isolated as such, but oxidised to sulphone by potassium permanganate.

β-Phenylsulphonepropionic acid, $SO_2Ph\cdot CH_2\cdot CH_2\cdot CO_2H$, obtained by the union of acrylic acid and thiophenol in glacial acetic acid during four weeks, crystallises from dilute alcohol in white leaflets, m. p. 56—57°. The position of the phenylsulphone group and, inferentially, that of the other sulphone groups, is shown to be the β by the preparation of β-phenylsulphone-β-phenylpropionic acid from cinnamic acid and thiophenol (compare Kohler and Reimer, Abstr., 1904, i, 234). The *silver* salt, $C_{15}H_{13}O_4SAg$, is white, the *amide*, $C_{15}H_{15}O_3NS$, crystallises from water, m. p. 123—124°, and the *anilide*, $C_{21}H_{19}O_3NS$, has m. p. 157—158°. The *ethyl* ester, $C_{17}H_{18}O_4S$, forming white needles, m. p. 54—55°, is prepared from the acid; it could not be obtained from ethyl cinnamate and thiophenol. *β-Ethylsulphone-β-phenylpropionic acid*, $SO_2Et\cdot CHPh\cdot CH_2\cdot CO_2H$, forms white crystals, m. p. 139—140°. The influence of the phenyl group in the β-position is to facilitate the addition; when the phenyl is also in the α-position, addition still occurs, but the α-phenylcinnamic acid and thiophenol have to be heated in a solution of glacial acetic acid, saturated with hydrogen chloride, under pressure for seven hours at 130°. The *β-phenylsulphone-αβ-diphenylpropionic acid*, $SO_2Ph\cdot CHPh\cdot CHPh\cdot CO_2H$, so derived crystallises from alcohol; m. p. 233—234°. The inference is drawn that as stilbene does not form an additive compound with thiophenol, the carboxyl group exercises an influence. It is noteworthy that neither α-methyl- nor α-ethyl-cinnamic acid give products with thiophenol, and all three α-substituted cinnamic acids are not reactive towards ethyl mercaptan. Further, β-furfurylacrylic acid and mercaptans could not be made to unite.

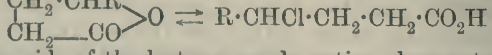
No additive product is obtained when *o*-nitrocinnamic acid and thiophenol are heated under pressure in glacial acetic acid solution saturated with hydrogen chloride at 100° for nine hours, but, when heated at 110° for eighteen hours, *β-phenylsulphone-β-*o*-nitrophenyl propionic acid*, $NO_2\cdot C_6H_4\cdot CH(SO_2Ph)\cdot CH_2\cdot CO_2H$, is finally obtained as yellow crystals, m. p. 157—160°; the corresponding meta- and para-derivatives have m. p. 170° and 197—200° respectively. *β-Phenylsulphone-*o*-tolylpropionic acid*, $SO_2Ph\cdot CH(C_6H_4Me)\cdot CH_2\cdot CO_2H$, obtained in a similar manner to the nitro-compounds, forms white, rectangular plates, m. p. 164—165°; the m-*tolyl* and p-*tolyl* derivatives have m. p. 235—236° and 210°. W. R.

Action of Potassium Hypochlorite on Cinnamamide. II. R. A. Weermann (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, **10**, 308—309. Compare Abstr., 1907, i, 132).—The action of an alkaline solution of potassium hypochlorite on a methyl-alcoholic solution of cinnamamide results in the formation of methyl styrylcarbamate, b. p. 181—182°/14 mm.; m. p. 122—123° (corr.). Thiele and Pickard (Abstr., 1900, i, 29) give m. p. 115°. When similarly treated, o-nitrocinnamamide yields *methyl* o-*nitrostyrylcarbamate*,

$$NO_2\cdot C_6H_4\cdot CH\!:\!CH\cdot NH\cdot CO_2Me,$$

bright yellow needles, m. p. 149—150°. W. H. G.

The Synthesis of Substituted Aromatic Acids. III. Johan F. Eykman (*Chem. Weekblad*, 1907, **4**, 727—738. Compare Abstr., 1904, i, 669; 1905, i, 528.)—Aliphatic lactonic acids, such as hexylparaconic acid, do not react with aromatic hydrocarbons in presence of aluminium chloride, even when the mixture is maintained at 40—50° for several weeks, indicating that the possibility of condensation depends on the nature of the group attached to the lactone ring. Since γ-cyanovalerolactone is also unaffected by these reagents, the non-reactivity cannot be due to the union of the CO_2H-group in hexylparaconic acid with the β-C-atom. Although monochloroacetic acid does not form condensation products by the Friedel and Crafft reaction, γ-chlorobutyric acid, like γ-butyrolactone (Abstr., 1907, i, 378), condenses with benzene and toluene to form γ-phenylbutyric acid and γ-tolylbutyric acid respectively, indicating that the γ-halogen-substituted acid is an intermediate product. The non-reactivity of hexylparaconic acid and γ-valerolactone is explained by the fact that when the equilibrium in the reversible reaction :

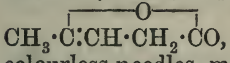


$$\left.\begin{array}{l}CH_2\cdot CHR\\ CH_2\text{——}CO\end{array}\right\rangle O \rightleftarrows R\cdot CHCl\cdot CH_2\cdot CH_2\cdot CO_2H$$

is greater on the side of the lactone, condensation does not take place. The condensation of Δ^{β}-acids supports the view of the intermediate production of hydrogen chloride additive products in the condensation with lactones.

Δ^{β}-Phenylcrotonic acid condenses with benzene to form $\gamma\gamma$-diphenylbutyric acid (m. p. 107°), identical with that obtained from phenylbutyrolactone (Abstr., 1904, i, 669) and by reduction of dichloro- and dibromo-diphenylcrotonic acids (Hill and Dunlap, Abstr., 1897, i, 572). It is uncertain whether $\beta\gamma$-diphenylcrotonic acid is also formed.

Allylacetic acid yields with benzene, γ-phenylvaleric acid, a non-crystallisable liquid, unlike that (m. p. 13°) obtained from the isomeric valerolactone. The difference may be due to the presence of a small proportion of δ-phenylvaleric acid.

Δ^{β}-Hydrosorbic acid, $CH_3\cdot CH_2\cdot CH\colon CH\cdot CH_2\cdot CO_2H$, yields with benzene a liquid acid, probably a mixture of γ- and β-phenylhexoic acids. Allylcyanide gives with benzene a nitrile, possibly a mixture of γ- and β-phenylbutyronitriles, which hydrolyses to an oily acid, partly crystalline (m. p. about 50°. γ-Phenylbutyric acid melts at 51·7°). Δ^{β}- and Δ^{α}-Hydropiperic acids resinify. Allylmalonic acid does not form an aromatic substituted acid, so that an α-CO_2H, like a β-CO_2H and a γ-CN group, prevents the condensation. α-Angelolactone,  $CH_3\cdot\overbrace{C\colon CH\cdot CH_2\cdot C}^{O}O$, yields with benzene, $\gamma\gamma$-diphenylvaleric acid, colourless needles, m. p. 115°, and with toluene an oil,

$$CH_3\cdot C(C_7H_7)\colon CH\cdot CH_2\cdot CO_2H.$$

β-Campholenic acid gives with benzene, β-phenyldihydrocampholenic acid, colourless crystals, m. p. about 90°, b. p. 190° (4 mm.). Crotonic acid yields with benzene a syrupy acid (b. p. 280°), possibly a mixture of α- and β-phenylbutyric acids.

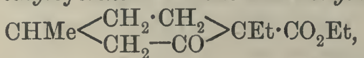
*iso*Lauronolic acid and benzene give a phenyldihydro*iso*lauronolic acid, colourless crystals (m. p. 119°), different from that obtained by Burcker (Abstr., 1895, i, 108) from camphoric anhydride, but probably having the constitution assigned by Blanc (Abstr., 1900, i, 329) to Burcker's acid.

The action of toluene and of anisole on camphoric anhydride is also under examination. A. J. W.

β-Phenylcinnamic Acid ($\beta\beta$-Diphenylacrylic Acid). Hans Rupe and E. Busolt (*Ber.*, 1907, 40, 4537—4540. Compare Kohler and Johnstin, Abstr., 1905, i, 215).—*Ethyl β-hydroxy-$\beta\beta$-diphenylpropionate*, $OH\cdot CPh_2\cdot CH_2\cdot CO_2Et$, is readily obtained by the action of dilute acid on the product formed by the condensation of benzophenone, ethyl bromoacetate, and zinc in the presence of benzene. It crystallises from dilute alcohol in glistening prisms, m. p. 87°. The corresponding *acid*, $C_{15}H_{14}O_3$, obtained by hydrolysing the ester with methyl-alcoholic potash, crystallises from dilute alcohol in pearly needles, m. p. 212°, and, when heated with sodium acetate and acetic anhydride, yields β-phenylcinnamic acid, m. p. 162° (Kohler and Johnstin, 155°). It can be distilled without decomposition at atmospheric pressure. The *ammonium*, *magnesium*, and *calcium* salts are somewhat sparingly soluble. When oxidised, the acid yields benzophenone. J. J. S.

Syntheses by Means of the Carboxylic Esters of Cyclic Ketones. VII. Influence of the Alkyl Groups on the Synthesis and Degradation of 1-Alkyl*cyclo*hexane-2-one-1-carboxylic Esters. Arthur Kötz [and, in part, Arthur Bieber, Leopold Hesse, and Adolf Schwarz] (*Annalen*, 1907, **357**, 192—208. Compare Abstr., 1906, i, 58, 59).—It has been shown in the previous parts of this investigation that the alkylation of *cyclo*pentane- and *cyclo*hexane-2-one-1-carboxylic esters by means of sodium ethoxide and an alkyl iodide takes place with diminishing velocity, as does also the ketonic and acid hydrolyses of the resulting alkyl derivative, as the weight of the alkyl increases. These generalisations are further illustrated in the present paper in the case of ethyl methyl*cyclo*hexane-3-one-4-carboxylate (Kötz and Hesse, Abstr., 1906, i, 88) and its derivatives.

Ethyl 1-*methyl*-4-*ethyl*cyclo*hexane*-3-*one*-4-*carboxylate*,



$$\mathrm{CHMe}\left<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2{-}CO}\end{matrix}\right>\mathrm{CEt\cdot CO_2Et},$$

b. p. 126°/10 mm., prepared by the action of ethyl iodide on the potassium derivative of ethyl methyl*cyclo*hexane-3-one-4-carboxylate in xylene, forms a *semicarbazide*, $C_{13}H_{23}O_3N_3$, crystallising in white needles, m. p. 160°.

Ethyl 1-methyl-4-*iso*propyl*cyclo*hexane-3-one-4-carboxylate is prepared best by heating the potassium derivative of the same ester with *iso*propyl chloride in xylene under pressure at 120°.

When boiled with alcoholic potassium hydroxide, the *cyclo*hexane-2-one-1-carboxylic esters yield *cyclo*hexane-2-ones; in this manner, 1 : 4-dimethyl*cyclo*hexane-2-one has been obtained from ethyl 1 : 4-dimethyl*cyclo*hexane-2-one-1-carboxylate (Kötz and Hesse, *loc. cit.*), and 1-methyl-4-ethyl*cyclo*hexane-3-one (Haller, Abstr., 1905, i, 214) from ethyl 1-methyl-4-ethyl*cyclo*hexane-3-one-4-carboxylate.

Substituted pimelic esters are formed by boiling *cyclo*hexane-2-one-1-carboxylic esters with sodium ethoxide in alcoholic solution. The following three esters have been prepared in this manner.

Ethyl αδ-*dimethylpimelate*, $CO_2Et\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2Et$, b. p. 152—153°/12 mm., from ethyl 1 : 4-dimethyl*cyclo*hexane-2-one-1-carboxylate, on hydrolysis with dilute hydrochloric acid, yields αδ-*dimethylpimelic acid*; the *silver* salt, $C_9H_{14}O_4Ag_2$, was analysed.

Ethyl δ-*methyl*-α-*ethylpimelate*,

$$CO_2Et\cdot CHEt\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2Et,$$

from ethyl 1-methyl-4-ethyl*cyclo*hexane-3-one-4-carboxylate, is obtained as a colourless oil, b. p. 142—144°/10 mm., and, on hydrolysis with methyl-alcoholic potassium hydroxide, yields δ-*methyl*-α-*ethylpimelic acid*, which forms a hygroscopic, brown mass; the *silver* salt, $C_{10}H_{16}O_4Ag_2$, was analysed.

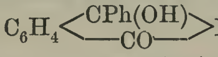
Ethyl δ-*methyl*-α-iso*propylpimelate*,

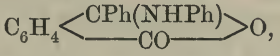
$$CO_2Et\cdot CHPr^{\beta}\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2Et,$$

from ethyl 1-methyl-4-*iso*propyl*cyclo*hexane-3-one-4-carboxylate, is obtained as a transparent liquid, b. p. 151—153°/9 mm., and, on hydrolysis with methyl-alcoholic potassium hydroxide, yields the corresponding *acid*; the *silver* salt, $C_{11}H_{18}O_4Ag_2$, was analysed.

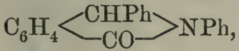
G. Y.

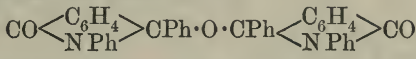
Acid-anilides, Anilo-acids, and ψ-Anilides. HANS MEYER (*Monatsh.*, 1907, 28, 1211—1230).—The numerous isomeric condensation products with primary bases of the type of aniline, which can be derived theoretically from *o*-aldehydo- and keto-acids by elimination of water from the components, have been studied previously in the aromatic series only in the case of the aldehydo-acids. The present paper contains an account of the substances obtained by the action of aniline on benzoylbenzoic acids.

o-Benzoylbenzoic acid reacts with aniline, forming, chiefly, o-*benzoylbenzoyl-ψ-anilide*,  $\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CPh(OH)}\\ \mathrm{CO}\end{matrix}{>}\mathrm{NPh}$ or, less probably,



$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CPh(NHPh)}\\ \mathrm{CO}\end{matrix}{>}\mathrm{O},$$

which crystallises from acetone in colourless leaflets, m. p. 221°, dissolves in hot dilute alkalis, forming a slightly yellow solution, behaves as a ψ-acid on titration with potassium hydroxide in presence of phenolphthalein, and forms an oily, yellow *potassium* salt. When dissolved in alkalis and precipitated by acids, the ψ-anilide forms a *hydrate*, which may have the structure: $\mathrm{NHPh{\cdot}CPh(OH){\cdot}C_6H_4{\cdot}CO_2H}$. It separates in colourless crystals, m. p. about 195°, loses only traces of water when heated in a steam-bath, and can be recrystallised unchanged from solvents boiling at low temperatures, but, on recrystallisation from boiling alcohol or glacial acetic acid, loses H_2O, forming the ψ-anilide, m. p. 221°. Reduction of the ψ-anilide with zinc and acetic acid leads to the formation of *phenylphthalideanilide*,  $\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CHPh}\\ \mathrm{CO}\end{matrix}{>}\mathrm{NPh}$, which is formed also by heating phenylphthalide with aniline and aniline hydrochloride; it separates from methyl alcohol in dull crystals, m. p. 195°, becomes electrified when rubbed, and gives Tafel's anilide reaction.

A *substance*,  $\mathrm{CO}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{NPh}\end{matrix}{>}\mathrm{CPh{\cdot}O{\cdot}CPh}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{NPh}\end{matrix}{>}\mathrm{CO}$, formed as a by-product in the action of aniline on *o*-benzoylbenzoic acid, crystallises from alcohol in needles, m. p. 196°, is insoluble in aqueous alkalis, forms an intense orange-yellow solution in concentrated sulphuric acid, and, like the ψ-anilide, does not give Tafel's anilide reaction.

p-Benzoylbenzoic acid forms only a salt when heated with aniline. The *anilide*, $\mathrm{COPh{\cdot}C_6H_4{\cdot}CO{\cdot}NHPh}$, is prepared by the action of *p*-benzoylbenzoyl chloride on aniline; it crystallises in needles, m. p. 171°, and gives a bluish-red coloration with concentrated sulphuric acid and potassium dichromate.

o-*Benzoylbenzoylanilide*, formed together with the ψ-anilide by heating *o*-benzoylbenzoyl chloride containing small amounts of thionyl chloride with aniline in benzene solution, separates from acetic acid in colourless crystals, m. p. 195°, and gives a red coloration with concentrated sulphuric acid. A mixture of this anilide with the substance, m. p. 195°, obtained as a by-product in the preparation of the ψ-anilide from the acid, commences to sinter at 160°, m. p. 170°. The anilide is considered to be a secondary product of the action of benzoylbenzoyl chloride or of the thionyl chloride on the ψ-anilide, as this is transformed into the anilide when treated with thionyl chloride, acetyl chloride, or boiling acetic anhydride. Reduction of the anilide by means of zinc and acetic acid leads to formation of phenylphthalide.

When boiled with acetic anhydride, opianyl-ψ-anilide, which does not behave as a ψ-acid on titration, is transformed into *opianylanilide*, m. p. 179°, which is insoluble in alkalis, and gives a rosaniline red with concentrated sulphuric acid.

Acetophenonecarboxylic acid reacts with aniline, forming a crystalline *substance*, m. p. 203°, which is not identical with the product of the action of phthalylacetic acid on aniline. G. Y.

Determination of the Constitution of Isomeric Derivatives of *o*-Keto-acids. Hans Meyer (*Monatsh.*, 1907, 28, 1231—1237).—From the discovery of isomeric esters of aromatic *o*-keto-acids has arisen amongst others the question whether such isomerism is limited to the ortho-series or may possibly occur in the meta- and para-series. Whilst it is difficult to establish a conclusion based only on negative evidence, it seemed of importance to show in a special case that the present methods of investigation give no indication of such isomerism. There remains then to be determined the constitution of the representatives of each series of derivatives as also of the free acids.

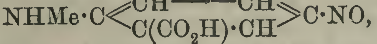
Methyl *p*-benzoylbenzoate, m. p. 107°, is obtained from *p*-benzoylbenzoic acid by all methods of esterification. *p*-Benzoylbenzoic acid does not form a mixed anhydride with acetic acid as does the *o*-acid.

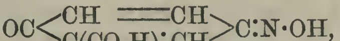
The action of methyl sulphate on *o*-benzoylbenzoyl-ψ-anilide in alkaline solution, $NHPh\cdot CPh(OH)\cdot C_6H_4\cdot CO_2K$, leads to the formation of an *ester*, which forms greenish-yellow crystals, m. p. 132°, and must have the constitution: $NPh{:}CPh\cdot C_6H_4\cdot CO_2Me$; when heated with 10% acetic acid, it yields methyl benzophenone-*o*-carboxylate, $COPh\cdot C_6H_4\cdot CO_2Me$, which is identical with Plaskuda's ester, m. p. 52°. The constitution of this ester establishes, also, the constitutions of its isomerides and analogues.

Whilst the action of *o*-benzoylbenzoyl chloride, prepared by means of thionyl chloride, on aniline leads to the formation of a mixture of the anilide and ψ-anilide, the former only is obtained from aniline and the crystalline acid chloride prepared by means of phosphorus pentachloride.

The normal esters of both *p*-aldehydo- and *o*-keto-acids are formed by means of diazomethane or of the silver salt, and usually melt at a lower temperature than the ψ-esters. But whilst the action of thionyl chloride on the *o*-aldehydo-acids leads to the formation of normal acid chloride, the ψ-acid chloride is formed by the action of thionyl chloride on *o*-benzoylbenzoic acid. Wegscheider (Abstr., 1906, i, 86) considers the free *o*-aldehydo-acids to have in aqueous solution a ψ-structure. Acids of the type of *o*-benzoylbenzoic acid, on the other hand, must have the normal structure. Such acids, however, undergo transformation readily with changes of temperature. Although at higher temperatures *o*-benzoylbenzoic acid forms the ψ-anilide, at the ordinary temperature it is a strong acid, having the conductivity constant $100k = 0{\cdot}0379$ with $v = 1024$, or $0{\cdot}0358$ with $v = 2048$; $\mu_\infty = 374{\cdot}5$.

G. Y.

Benzoquinoneoximecarboxylic Acid. JOSEF HOUBEN and WALTER BRASSERT (*Ber.*, 1907, 40, 4739—4743).—The authors have prepared benzoquinoneoximecarboxylic acid from 5-*nitroso*-N-*methylanthranilic acid*,  $\mathrm{NHMe\cdot C}\Big<\substack{\mathrm{CH{-\!-\!-}CH}\\ \mathrm{C(CO_2H)\cdot CH}}\Big>\mathrm{C\cdot NO}$, which is obtained from *o*-nitrosomethylaminobenzoic acid, $\mathrm{CO_2H\cdot C_6H_4\cdot N(NO)Me}$, and alcohol or glacial acetic acid containing hydrogen chloride. The precautions to be observed in the isolation of the free acid from its hydrochloride are described. The acid separates from alcohol in dark green prisms with a blue lustre or in needles; it separates from glacial acetic acid in green needles. It begins to decompose about 100°; when reduced, it forms a colourless compound, which very quickly becomes blue.

Benzoquinoneoximecarboxylic acid,  $\mathrm{OC}\Big<\substack{\mathrm{CH{=\!=\!=}CH}\\ \mathrm{C(CO_2H){:}CH}}\Big>\mathrm{C{:}N\cdot OH}$, obtained by boiling 5-nitroso-*N*-methylanthranilic acid with aqueous sodium carbonate, has m. p. 162—163°; it crystallises from benzene in dark green scales, and from water, when crystallised quickly, in dark green needles. Its aqueous solution decomposes when filtered through ordinary filter paper. The acid decomposes on contact with air. It reacts with phenylhydrazine, semicarbazide, hydroxylamine, and aniline respectively. A. McK.

Hydropinenealdehyde. JOSEF HOUBEN and HANS DOESCHER (*Ber.* 1907, 40, 4576—4579).—With the object of comparing derivatives of pinene hydrochloride and bornyl chloride with derivatives of *iso*bornyl chloride, the author has prepared hydropinenealdehyde, $\mathrm{C_{10}H_{17}\cdot CHO}$. For this purpose, methylformanilide was obtained by boiling methylaniline with anhydrous formic acid for six hours; it has b. p. 263°/760 mm. and 121°/11 mm. It was then boiled for eight hours with magnesium pinene hydrochloride (Houben, Abstr., 1906, i, 21), when the following reaction takes place: $\mathrm{C_{10}H_{17}MgCl + CHO\cdot NMePh = C_{10}H_{17}\cdot CH(OMgCl)\cdot NMePh}$. The resulting magnesium compound, when decomposed in the usual manner, forms methylaniline hydrochloride and hydropinene aldehyde: $\mathrm{C_{10}H_{17}\cdot CH(OMgCl)\cdot NMePh} \longrightarrow \mathrm{C_{10}H_{17}\cdot CH(OH)\cdot NMePh} \longrightarrow \mathrm{C_{10}H_{17}\cdot CHO + NHMePh,HCl}$. *Hydropinenealdehyde*, isolated by aid of its sodium hydrogen sulphite compound, has an odour of camphor, undergoes oxidation with remarkable ease, and is very volatile with steam; m. p. above 120°, but indefinite, owing to the rapid oxidation of the aldehyde. Its *oxime*, $\mathrm{C_{10}H_{17}\cdot CH{:}N\cdot OH}$, crystallises from light petroleum is needles, has m. p. 60—61°, and b. p. 143°/13 mm.

The *semicarbazone*, $\mathrm{C_{10}H_{17}\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2}$, separates from benzene in small needles, m. p. 220°. A. McK.

Action of Organo-magnesium Pyridine Compounds on Aldehydes. BERNARDO ODDO (*Gazzetta*, 1907, 37, ii, 356—366).—The interaction of benzaldehyde and the pyridine compound of magnesium methyl iodide (compare Abstr., 1904, i, 920) yields: (1) styrene; (2) phenylmethylcarbinol, and (3) the *ether*, $\mathrm{O(CHPhMe)_2}$, b. p. 240—245°/20 mm., D^{28} 1·1154, which has the normal molecular weight in freezing benzene, and when heated or treated with 10% potassium hydroxide solution yields a crystalline *compound*, m. p. 90—92°, or 95°, according to its method of preparation.

The action of the pyridine compound of magnesium phenyl bromide on benzaldehyde yields: benzyl alcohol, benzyl ether, tetraphenylethane, diphenylcarbinol, and the ether, $O(CHPh_2)_2$. T. H. P.

Syntheses of Aromatic Aldehydes. II. The Hydrogen Cyanide Method. LUDWIG GATTERMANN (*Annalen*, 1907, **357**, 313—383. Compare Abstr., 1906, i, 589).—The hydrogen cyanide method for the synthesis of aromatic aldehydes permits of the introduction of the aldehydo-group, CHO, into phenols, ethers, or other derivatives of phenols. The aldehydo-group is introduced into monohydric phenols in the para-position to the hydroxyl if this is occupied by hydrogen, the *p*-hydroxy-aldehydes being formed in 50% to 90% yields. If the para-position is already occupied by a substituting group, *o*-hydroxy-aldehydes are formed in small yields in the benzene series, but readily in the β-naphthols. The dihydric phenols with the hydroxyls in the meta-position to each other, and dihydroxynaphthalenes with both hydroxyls in β-positions, readily yield aldehydes with the aldehydo-group in the ortho-position to one of the hydroxyls. Catechol and quinol, on the other hand, yield only small amounts of an aldehyde, or do not undergo the reaction. Also, in the case of the trihydric phenols, pyrogallol, and hydroxyquinol, the aldehydo-group is readily introduced into the ortho-position to one, or in phloroglucinol to two, of the hydroxyls.

In the ethers of the phenols, the alkyloxy-groups have a similar, but weaker, effect on the orientation of the aldehydo-group. Thus the monomethyl ethers of the *m*-dihydroxybenzenes yield *p*-hydroxy-*o*-methoxy-aldehydes. The ethers of catechol readily form aldehydes, differing in this from the free phenol. Two aldehydo-groups are introduced only into the ethylene and trimethylene ethers of monohydric phenols and naphthols, and into dialkyloxydiphenyls.

Directions are given for the preparation of anhydrous hydrogen cyanide; this is condensed with the phenol in ethereal solution by means of hydrogen chloride alone or together with zinc chloride, or with phenols or phenol ethers in benzene solution, or in absence of a solvent, by means of aluminium chloride and hydrogen chloride. The following new aldehydes are described.

Hydroxytolualdehyde [Me : CHO : OH = 1 : 3 : 4], m. p. 56°, prepared from *p*-cresol, is volatile in steam; the *azine*, $C_{16}H_{16}O_2N_2$, crystallises in yellow needles, m. p. 232°.

p-*Hydroxy*-m-*ethylbenzaldehyde*, $C_9H_{10}O_2$, prepared from *o*-ethylphenol, crystallises in colourless needles, m. p. 172—173°; the *azine*, $C_{18}H_{20}O_2N_2$, forms yellow needles, m. p. 262°.

4-*Hydroxy*-2 : 5-*dimethylbenzaldehyde*, from *p*-xylenol in an 80% yield, crystallises in colourless needles, m. p. 132—133°. The *oxime*, $C_9H_{11}O_2N$, colourless needles, m. p. 155°; the *phenylhydrazone*, colourless leaflets, m. p. 164°; the *azine*, $C_{18}H_{20}O_2N_2$, yellow needles, m. p. 280° (decomp.); the *condensation product* with aniline, $C_{15}H_{15}ON$, crystallises in colourless needles, m. p. 143°. When heated with aniline hydrochloride in alcoholic solution, the aldehyde forms the *hydrochloride* of an additive compound, $C_{15}H_{18}O_2NCl$, which crystallises in orange-red needles, decomp. about 240°. The action of the calculated amount of potassium nitrate on the aldehyde in concentrated sulphuric acid solution at $-10°$, leads to the formation of 3-*nitro*-4-*hydroxy*-2 : 5-*dimethylbenzaldehyde*, $C_9H_9O_4N$, crystallising in colourless leaflets, m. p. 188°; the *oxime*, $C_9H_{10}O_4N_2$, orange-red needles, decomp. 160°; the *azine*, $C_{18}H_{18}O_6N_4$, orange needles, decomp. 237°; the aniline *condensation product*, $C_{15}H_{14}O_3N_2$, forms ruby-red crystals with blue fluorescence, m. p. 136°. 4-*Hydroxy*-2 : 5-*dimethylcinnamic acid*, $C_{11}H_{12}O_3$, crystallises in colourless needles, m. p. 171°.

4-*Hydroxy*-2 : 3-*dimethylbenzaldehyde*, from 1 : 2 : 3-xylenol in a 60% yield, crystallises from toluene in colourless leaflets, m. p. 172°; the *phenylhydrazone*, $C_{15}H_{16}ON_2$, silvery scales, m. p. 165°; the *azine*, $C_{18}H_{20}O_2N_2$, yellow needles, m. p. 254°.

4-Hydroxy-3 : 5-dimethylbenzaldehyde, m. p. 115—116° (114°: Thiele and Eichwede, Abstr., 1900, i, 501), forms an *azine*, $C_{18}H_{20}O_2N_2$, crystallising in yellow needles, m. p. 262—263°.

4-*Hydroxy*-2 : 6-*dimethylbenzaldehyde*, from *s*-xylenol in an almost quantitative yield, crystallises in colourless needles, m. p. 189—190°. The *oxime*, colourless leaflets, m. p. 196°; the *azine*, yellow needles, m. p. 240°.

2-*Hydroxy*-4 : 5-*dimethylbenzaldehyde*, colourless leaflets, m. p. 70°, volatile with steam; the *phenylhydrazone*, colourless needles, m. p. 195°; the *azine*, yellow, crystalline powder, m. p. 317° (decomp.). On fusion with potassium hydroxide, the aldehyde yields 4 : 5-dimethylsalicylic acid, m. p. 199°.

p-Carvacrotaldehyde, m. p. 96°, formed from carvacrol and hydrogen cyanide by the aluminium chloride method, is identical with Nordmann's aldehyde (Abstr., 1885, 162). Lustig's aldehyde (Abstr., 1886, 346) is probably the *o*-aldehyde. The *phenylhydrazone* of the *p*-aldehyde, $C_{17}H_{20}ON_2$, crystallises in glistening leaflets, m. p. 109°; the *azine*, $C_{22}H_{28}O_2N_2$, yellow crystals, m. p. 238—240°; the *methyl ether*, b. p. 275°, formed by the action of potassium hydroxide and methyl iodide on the aldehyde, yields an *azine*, $C_{24}H_{32}O_2N_2$, yellow crystals, m. p. 184—185°, and on oxidation with alkaline permanganate is converted into the acid described by Gattermann and Obërlander (Abstr., 1899, i, 510).

When treated with hydrazine sulphate in dilute alcoholic solution, 1 : 4-hydroxynaphthaldehyde forms an *additive* compound,

$$OH\cdot C_{10}H_6\cdot CH(OH)\cdot NH\cdot NH\cdot CH(OH)\cdot C_{10}H_6\cdot OH,$$

which is obtained as a dark red substance, decomp. 220—236°, and when dissolved in alcohol loses water, forming the *azine*, $C_{22}H_{16}O_2N_2$, crystallising in yellow needles, m. p. 236°.

3-*Bromo*-4-*hydroxy*-1-*naphthaldehyde*, $C_{11}H_7O_2Br$, prepared by the action of bromine on 1 : 4-naphthaldehyde in cooled glacial acetic acid solution, crystallises in colourless needles, m. p. 145°, and forms *condensation products* with aniline, $C_{17}H_{12}ONBr$, leaflets, with red and green fluorescence, m. p. 180° (decomp.), with *p*-toluidine,

$$C_{18}H_{14}ONBr,$$

crystals with green and red lustre, m. p. 168°, and with *p*-xylidine, $C_{19}H_{16}ONBr$, red, monoclinic plates, m. p. 206° (decomp.).

With hydrogen cyanide and aluminium chloride in benzene solution, *ar*-tetrahydro-α-naphthol forms an *aldehyde*, $C_{11}H_{12}O_2$, which crystallises in yellow leaflets, m. p. 138—139°. The *condensation product* with aniline, $C_{17}H_{17}ON$, yellow to orange-red plates, m. p. 189°; the condensation product with *p*-toluidine, $C_{18}H_{19}ON$, yellow leaflets, m. p. 209—210°; the *azine*, $C_{22}H_{24}O_2N_2$, yellow needles, decomp. about 260°; the *methyl ether*, $C_{12}H_{14}O_2$, colourless needles, m. p. 58—59°.

2-*Chloro*-4-*hydroxybenzaldehyde*, $C_7H_5O_2Cl$, in a 50% yield, from *m*-chlorophenol, crystallises in colourless needles, m. p. 146·5°. The *oxime*, $C_7H_6O_2NCl$, stout crystals, m. p. 194°; the *azine*, $C_{14}H_{10}O_2N_2Cl_2$, yellow needles, m. p. 255° (decomp.).

2-*Bromo*-4-*hydroxybenzaldehyde*, formed in a 10% yield, crystallises in slightly yellow needles, m. p. 159·5°. The *oxime*, stout crystals, m. p. 128·5°, does not form an indoxazen derivative; the *azine*, needles, m. p. 260°.

Resorcylaldehyde condenses with aniline, forming a *product*, $C_{13}H_{11}O_2N$, crystallising in lemon-yellow needles, m. p. 131°. With aniline hydrochloride, the aldehyde forms an *additive* compound, $C_{13}H_{14}O_3NCl$, which crystallises in light yellow needles, and decomposes when heated. The *additive* compound, $C_{14}H_{14}O_5NCl$, formed with *p*-aminobenzoic acid in presence of hydrochloric acid, is obtained in yellow crystals, and decomposes when heated. The action of fuming nitric acid on the aldehyde in glacial acetic acid leads to the formation of 5-*nitro*-2 : 4-*dihydroxybenzaldehyde*, $C_7H_5O_5N$, which crystallises in yellowish-brown prisms, m. p. 148—149°. 3 : 5-*Dinitro*-2 : 4-*dihydroxybenzaldehyde*, $C_7H_4O_7N_2$, prepared by the action of fuming nitric acid on resorcylaldehyde, forms slightly yellow crystals, m. p. 170°. Both these aldehydes form intensely yellow or orange salts with alkalis, and give the typical aldehyde reactions; the crystalline derivatives mostly decompose when heated.

Chlororesorcylaldehyde, formed from chlororesorcinol, is obtained in the form of its *hydrate*, $C_7H_7O_4Cl$, which melts below 100°, and when more highly heated yields a sublimate of the aldehyde in colourless needles, m. p. 157°. The *oxime*, $C_7H_6O_3NCl$, colourless needles, m. p. 184°; the *azine*, $C_{14}H_{10}O_4N_2Cl_2$, yellow needles, m. p. above the b. p. of sulphuric acid; the *phenylhydrazone*, $C_{13}H_{11}O_2N_2Cl$, brownish-red needles, m. p. 185—193° (decomp.).

Cresorcylaldehyde, formed in a 90% yield from cresorcinol, crystallises from benzene in colourless needles, m. p. 146·5°. The *azine*, $C_{16}H_{16}O_4N_2$, yellow needles, m. p. 303° (decomp.).

1 : 5-*Dihydroxy*-4-*naphthaldehyde*, $C_{11}H_8O_3$, from 1 : 5-dihydroxynaphthalene, crystallises in yellow needles, m. p. 195—210°. 1 : 5-*Dihydroxy*-4-*naphthylideneaniline*, $C_{17}H_{18}O_2N$, forms dark red crystals, m. p. 195—196°.

2 : 7-*Dihydroxy*-1-*naphthaldehyde*, formed in an almost quantitative yield from 2 : 7-dihydroxynaphthalene, is obtained in the form of its *hydrate*, $C_{11}H_{10}O_4$, which crystallises in light yellow needles, m. p. 210—215° (decomp.), and over sulphuric acid in a vacuum, or more

quickly at 120°, loses H_2O, becoming yellowish-red. 2 : 7-*Dihydroxy*-1-*naphthylideneaniline*, $C_{17}H_{13}O_2N$, crystallises in golden needles, m. p. 195—196°, when quickly heated.

2 : 6-*Dihydroxy*-1-*naphthaldehyde*, $C_{11}H_8O_3$, crystallises in light yellow needles, m. p. 185—190° (decomp.). The *naphthylideneaniline*, $C_{17}H_{13}O_2N$, forms orange-red needles with green lustre, and is partially melted at 215°, but not completely at 235°. The *phenylhydrazone*, $C_{17}H_{14}O_2N_2$, crystallises in golden needles, and commences to decompose at 200°, m. p. about 230°.

Trihydroxybenzylideneaniline, $C_{13}H_{11}O_3N$, crystallises in ruby-red needles, m. p. 198°. The *additive* compound of pyrogallolaldehyde and aniline hydrochloride, $C_6H_2(OH)_3 \cdot CH(OH) \cdot NHPh,HCl$, crystallises in yellow needles, m. p. 245°, and when boiled with water is converted into the benzylideneaniline.

Dihydroxycoumarin diacetate, $C_{13}H_{10}O_6$, prepared by heating phloroglucinolaldehyde with acetic anhydride and sodium acetate at 160—170° under pressure, crystallises in needles, m. p. 138°, and when heated with dilute sulphuric acid yields *dihydroxycoumarin*, $C_9H_6O_4$, crystallising in yellow needles, m. p. above 250° (partial decomp.). The solutions of this are not fluorescent; it forms yellow *salts* with aqueous alkalis, ammonia, or calcium or barium hydroxide, and with aqueous ferric chloride gives a green coloration, becoming red, and a precipitate.

4-Hydroxy-2-methoxybenzaldehyde is formed in a 75% yield from resorcinol monomethyl ether, whilst anisaldehyde is obtained in an almost quantitative yield from anisole.

Orcinol monomethyl ether forms 4-*hydroxy*-6-*methoxy*-2-*methylbenzaldehyde*, $C_9H_{10}O_3$, which crystallises in colourless needles, m. p. 188°, and is not volatile with steam. The *oxime*, colourless needles, m. p. 127°; the *phenylhydrazone*, $C_{15}H_{16}O_2N_2$, yellow plates, m. p. 159°; the *azine*, $C_{18}H_{20}O_4N_2$, yellow leaflets, m. p. 253° (decomp.).

p-*Ethoxybenzaldehyde*, $C_9H_{10}O_2$, formed in an almost quantitative yield from phenetole, is obtained as a colourless oil, b. p. 249°, D_{21}^{21} 1·08, has a pleasant odour, and on oxidation with alkaline permanganate is converted into *p*-ethoxybenzoic acid. The *oxime*, $C_9H_{11}O_2N$, colourless needles, m. p. 83°; the *azine*, $C_{18}H_{20}O_2N_2$, crystallises in yellow leaflets, m. p. 172°, forming a turbid liquid, clearing at 197°; the *condensation product* with benzidine, $C_{30}H_{28}O_2N_2$, crystallises in yellow leaflets, m. p. 248° to a turbid liquid, clearing when heated above the b. p. of sulphuric acid.

3-*Chloro*-4-*methoxybenzaldehyde*, $C_8H_7O_2Cl$, from *o*-chloroanisole, crystallises in colourless needles, m. p. 53°, and on oxidation yields 3-chloro-4-methoxybenzoic acid. The *oxime*, $C_8H_8O_2NCl$, forms colourless needles, m. p. 115°.

2-Chloro-4-methoxybenzaldehyde, from *m*-chloroanisole, is identical with Tiemann's aldehyde (Abstr., 1891, 704).

2-*Chloro*-4-*ethoxybenzaldehyde*, from *m*-chlorophenetole, crystallises in colourless needles, m. p. 66·5°. The *oxime*, $C_9H_{10}O_2NCl$, colourless needles, m. p. 89·5°.

2-*Bromo*-4-*ethoxybenzaldehyde*, from *m*-bromophenetole, crystallises in colourless needles, m. p. 69·5°.

4-*β-Bromoethoxybenzaldehyde*, $CH_2Br\cdot CH_2\cdot O\cdot C_6H_4\cdot CHO$, formed in a 50% yield from β-bromoethoxybenzene, crystallises in colourless needles, m. p. 52°. The *oxime*, $C_9H_{10}O_2NBr$, colourless leaflets, m. p. 108°; the *phenylhydrazone*, $C_{15}H_{15}ON_2Br$, silvery needles, m. p. 127°; the *azine*, $C_{18}H_{18}O_2N_2Br_2$, yellow needles, m. p. 176·5°. 4-*β-Bromoethoxybenzoic acid*, $C_9H_9O_3Br$, prepared by oxidation of the aldehyde with permanganate in alkaline solution, crystallises in needles, m. p. 177°. When heated with potassium acetate and absolute alcohol at 150° under pressure, the bromo-aldehyde is converted into p-*β-hydroxyethoxybenzaldehyde*, $OH\cdot CH_2\cdot CH_2\cdot O\cdot C_6H_4\cdot CHO$, which crystallises in colourless needles, m. p. 34°; the *oxime*, $C_9H_{11}O_3N$, colourless needles, m. p. 98—99°; the *phenylhydrazone*, $C_{15}H_{16}O_2N_2$, colourless needles, m. p. 102—103°; the *azine*, $C_{18}H_{20}O_4N_2$, light yellow needles, m. p. 184°, forming a turbid liquid, and clearing at 207°.

Methoxytolualdehyde [Me:CHO:OMe = 1 : 3 : 6], b. p. 251° (Abstr., 1898, 476), is prepared from *o*-tolyl methyl ether; the *oxime*, $C_9H_{11}O_2N$, m. p. 68—70°, is formed together with traces of its *stereoisomeride*; the *azine*, $C_{18}H_{20}O_2N_2$, yellow, nacreous leaflets, m. p. 172—173°. The corresponding 4-ethoxy-aldehyde (*loc. cit.*) crystallises from light petroleum in glistening needles, m. p. 33—34°; the *oxime*, colourless needles, m. p. 92—93°; the *azine*, $C_{20}H_{24}O_2N_2$, yellow leaflets, m. p. 155—156°; the *condensation product* with benzidine, $C_{32}H_{32}O_2N_2$, yellow leaflets, m. p. 238°, forming a turbid liquid.

o-*Tolyl β-bromoethyl ether*, $C_9H_{11}OBr$, solidifies at −90°, b. p. 213—125°/9 mm. *β-Bromoethoxy*-m-*tolualdehyde*, $C_{10}H_{11}O_2Br$ [Me : CHO : C_2H_4Br = 1 : 3 : 6], crystallises in colourless needles, m. p. 39°; the *oxime*, $C_{10}H_{12}O_2NBr$, colourless needles, m. p. 73°; the *azine*, $C_{20}H_{22}O_2N_2Br_2$, yellow needles, m. p. 136°. 6-*β-Hydroxyethoxy*-m-*tolualdehyde*, $OH\cdot CH_2\cdot CH_2\cdot O\cdot C_6H_3Me\cdot CHO$, prepared by the action of potassium acetate and alcohol on the β-bromo-compound, crystallises from benzene in slightly yellow needles, m. p. 61—62°; the *oxime*, $C_{10}H_{13}O_3N$, colourless needles, m. p. 115°; the *azine*, yellow needles, m. p. 184°.

Methoxytolualdehyde [Me : CHO : OMe = 1 : 2 : 5], b. p. 257° (Abstr., 1898, i, 477), on oxidation, yields *m*-homoanisic acid; the *oxime*, $C_9H_{11}O_2N$, colourless needles, m. p. 81°; the *azine*, golden needles, m. p. 141°; the *condensation product* with benzidine, $C_{30}H_{28}O_2N_2$, yellow leaflets, m. p. 171°, forming a turbid liquid, which clears above the b. p. of sulphuric acid.

Ethoxytolualdehyde [Me : CHO : OEt = 1 : 2 : 5], from *m*-tolyl ethyl ether, forms a strongly refracting, colourless oil, b. p. 260—262°; the *oxime*, $C_{10}H_{13}O_2N$, stout crystals, m. p. 84°; the *azine*, golden leaflets, m. p. 142°; the *condensation product* with benzidine, $C_{32}H_{32}O_2N_2$, golden leaflets, m. p. 167° (turbid), clears above 300°.

Methoxytolualdehyde [Me : CHO : OMe = 1 : 3 : 4], b. p. 250° (Abstr., 1898, i, 477), prepared from *m*-tolyl methyl ether, contains a small amount of the *isomeride* [Me : CHO : OMe = 1 : 2 : 4], since, on oxidation, it yields an acid, m. p. 67°, accompanied by traces of a more sparingly soluble acid, m. p. 192—193°. The *oxime*, $C_9H_{11}O_2N$, colourless needles, m. p. 144—145°.

Ethoxytolualdehyde [Me : CHO : OEt = 1 : 3 : 4], from *p*-tolyl ethyl ether, crystallises from light petroleum in colourless needles, m. p. 32—33° ; the *oxime*, $C_{10}H_{13}O_2N$, colourless needles, m. p. 87° ; the *azine*, yellow prisms, m. p. 154—155°.

4-*Methoxy*-2 : 6-*dimethylbenzaldehyde*, $C_{10}H_{12}O_2$, prepared from s-*xylenyl methyl ether*, b. p. 194·5°, crystallises in colourless needles, m. p. 18°, b. p. 271—272° ; the *oxime*, colourless leaflets, m. p. 121·5°. s-*Xylenyl ethyl ether*, b. p. 208°, yields 4-*ethoxy*-2 : 6-*dimethylbenzaldehyde*, m. p. 279—280°, which does not solidify when cooled ; the *oxime*, colourless needles, m. p. 100°. v-m-*Xylenyl methyl ether*, b. p. 182—183°, yields chiefly 4-hydroxy-3 : 5-dimethylbenzaldehyde, m. p. 116°, together with small amounts of the corresponding *methoxyaldehyde*, $C_{10}H_{12}O_2$, b. p. 257°. v-m-*Xylenyl ethyl ether*, b. p. 194·5°, yields only moderate amounts of 4-*ethoxy*-3 : 5-*dimethylbenzaldehyde*, b. p. 265·5°.

4-*Phenoxybenzaldehyde*, $OPh\cdot C_6H_4\cdot CHO$, from phenyl ether, solidifies in a freezing mixture, b. p. 191—193°/22 mm., and on oxidation with alkaline permanganate yields *p*-phenoxybenzoic acid. The *oxime*, $C_{13}H_{11}O_2N$, crystalline powder, m. p. 86° ; the *azine*, sulphur-yellow leaflets, m. p. 143° ; the *phenylhydrazone*, yellow leaflets, m. p. 123°.

4-*Methoxy*-1-*naphthaldehyde*, prepared by boiling 1 : 4-hydroxynaphthaldehyde with methyl iodide and alcoholic potassium hydroxide, is obtained as a colourless liquid, b. p. 212°/40 mm., and, on oxidation, yields Gattermann and Hess's acid, m. p. 232° (Abstr., 1888, 574). With hydrazine sulphate, the aldehyde yields the *additive* compound, $OMe\cdot C_{10}H_6\cdot CH(OH)\cdot NH\cdot NH\cdot CH(OH)\cdot C_{10}H_6\cdot OMe$, which forms dark red needles, decomp. 160—182°, and, when heated with alcohol, loses $2H_2O$, forming the *azine*, $C_{24}H_{20}O_2N_2$, crystallising in light yellow needles, m. p. 182° ; this again forms the additive compound on treatment with mineral acids. The corresponding *ethoxy-aldehyde*, $C_{13}H_{12}O_2$, forms yellow crystals, m. p. 75° ; the *azine*, yellow needles, m. p. 209°.

2-*Methoxy*-1-*naphthaldehyde*, $C_{12}H_{10}O_2$, prepared from *β*-naphthyl methyl ether or 2-hydroxy-1-naphthaldehyde, crystallising in stout prisms, m. p. 83·5° ; the *azine*, $C_{24}H_{20}O_2N_2$, crystallises from nitrobenzene in golden prisms with blue lustre, m. p. 255—256°. The corresponding *ethoxy-aldehyde* crystallises from glacial acetic acid in long needles, m. p. 110° ; the *azine*, $C_{26}H_{24}O_2N_2$, golden crystals, m. p. 184°.

The aldehyde formed from veratrole crystallises in yellow needles, m. p. 43—44° (42° : Tiemann, this Journ., 1876, i, 76) ; the *oxime*, $C_9H_{11}O_3N$, forms spherical aggregates, m. p. 88—89° ; the *azine*, $C_{18}H_{20}O_4N_2$, yellow leaflets, m. p. 189—190° ; the *additive* compound with aniline hydrochloride, $C_6H_3(OMe)_2\cdot CH(OH)\cdot NHPh,HCl$, light yellow needles, m. p. 112°.

3 : 4-*Diethoxybenzaldehyde*, $C_6H_3(OEt)_2\cdot CHO$, prepared from catechol diethyl ether, is obtained as an oil, b. p. 278—280°, and, on oxidation, yields protocatechuic acid diethyl ether ; the *azine*, $C_{22}H_{28}O_4N_2$, yellow leaflets, m. p. 169—170°.

2 : 4-Dimethoxybenzaldehyde (Abstr., 1898, i, 477) forms an *oxime*,

$C_9H_{11}O_3N$, colourless needles, m. p. 106°, and an *azine*, $C_{18}H_{20}O_4N_2$, yellow needles, m. p. 195°.

2 : 5-*Dimethoxybenzaldehyde,* formed from benzoquinol dimethyl ether, crystallises in colourless needles, m. p. 53°. 2 : 5-*Diethoxybenzaldehyde*, colourless needles, m. p. 62·5°.

4 : 5-*Dimethoxy-2-methylbenzaldehyde,* $C_{10}H_{12}O_3$, formed from homocatechol dimethyl ether, crystallises in colourless needles, m. p. 76°, and, on oxidation, yields a *carboxylic acid,* $C_{10}H_{12}O_4$, crystallising in colourless needles, m. p. 146—147°, together with *m*-hemipinic acid. The *oxime,* $C_{10}H_{13}O_3N$, colourless needles, m. p. 124°; the *azine,* yellow, rhombic plates, m. p. 228°. The corresponding *methoxyethoxyaldehyde,* $C_{11}H_{14}O_3$, m. p. 33—34°, b. p. 293—294°; the *oxime,* colourless leaflets, m. p. 116·5°.

The *aldehyde* prepared from cresorcinol dimethyl ether, b. p. 211°, crystallises in colourless needles, m. p. 116·5°; the *oxime,* $C_{10}H_{13}O_3N$, nacreous leaflets, m. p. 145°. The isomeric *aldehyde* from orcinol dimethyl ether forms colourless needles, m. p. 62°; the *azine,* $C_{10}H_{24}O_4N_2$, yellow leaflets, m. p. 193°; the *phenylhydrazone,* $C_{16}H_{18}O_2N_2$, yellow needles, m. p. 100—101°.

The *additive* compound of asarylaldehyde and aniline hydrochloride, $C_{16}H_{20}O_4NCl$, crystallises in orange-yellow needles, m. p. 188°.

Catechol ethylene ether, prepared by the action of potassium hydroxide and ethylene dibromide on catechol, is a colourless oil, b. p. 110—111°/31 mm. or 99—100°/17 mm., and has an aromatic odour. Contrary to Moureu's statement (Abstr., 1898, i, 644), catechualdehyde ethylene ether has no odour; it is oxidised by permanganate, yielding protocatechuic acid ethylene ether, m. p. 135·5°. The *azine,* $C_{18}H_{16}O_4N_2$, forms yellow needles, m. p. 190—191°.

Ethylene ether of 4-*hydroxybenzaldehyde,* $C_2H_4(O{\cdot}C_6H_4{\cdot}CHO)_2$, prepared from phenyl ethylene ether, crystallises in colourless needles, m. p. 117—118°; the *aniline* derivative, $C_{28}H_{24}O_2N_2$, glistening leaflets, m. p. 183—184°; the *phenylhydrazone,* $C_{28}H_{26}O_2N_4$, brown leaflets, m. p. 217—218°. The corresponding *trimethylene ether,* $C_{17}H_{16}O_4$, crystallising in yellow needles, m. p. 135—136°, is formed from phenyl trimethylene ether, and also by the action of trimethylene dibromide on sodium *p*-hydroxybenzaldehyde; the *dioxime,* $C_{17}H_{18}O_4N_2$, colourless needles, m. p. 153—154°; the *disemicarbazone,* $C_{19}H_{22}O_4N_6$, colourless needles, m. p. 297—298°; the *azine,* $C_{17}H_{16}O_2N_2$, is obtained as a yellow, insoluble substance, m. p. above 360°, and is probably polymolecular.

Ethylene ether of 6-*hydroxy*-m-*tolualdehyde,* $C_2H_2(O{\cdot}C_6H_3Me{\cdot}CHO)_2$, crystallises in colourless needles, m. p. 150°; the *oxime,* yellow needles, m. p. 191—192°; the *phenylhydrazone,* $C_{30}H_{30}O_2N_4$, yellow crystals, m. p. 231°; the *aniline* derivative, $C_{30}H_{28}O_2N_2$, colourless needles, m. p. 161°; the p-*toluidine* derivative, $C_{32}H_{32}O_2N_2$, colourless needles, m. p. 156°. o-*Tolyl trimethylene ether,* $C_{17}H_{20}O_2$, forms a colourless oil, b. p. 225°/28 mm. or 341—343°/760 mm. The corresponding *di*-4 : 4′-*aldehyde,* $C_{19}H_{20}O_4$, crystallises in colourless needles, m. p. 114°.

Ethylene ether of 5-*hydroxy*-o-*tolualdehyde,* from m-*tolyl ethylene ether,* m. p. 91°, crystallises from glacial acetic acid in yellow leaflets,

m. p. 125—126°. p-*Xylenol ethylene ether*, $C_{18}H_{22}O_2$, crystallises in colourless needles, m. p. 82—83°, and forms a *dialdehyde*, $C_{20}H_{22}O_4$, obtained in a 66% yield and crystallising in colourless needles, m. p. 163°. *α-Naphthyl trimethylene ether*, $C_{23}H_{20}O_2$, crystallises in colourless needles, m. p. 103—104°. *Trimethylene ether* of 1 : 4-*hydroxynaphthaldehyde*, $C_{25}H_{20}O_4$, forms yellow needles, m. p. 159—160°; the *oxime*, $C_{25}H_{22}O_4N_2$, glistening leaflets, m. p. 192—193°; the *aniline* derivative, $C_{37}H_{30}O_2N_2$, is obtained as a yellow, crystalline precipitate, m. p. 188—189°. *β-Naphthyl trimethylene ether*, colourless leaflets, m. p. 148—149°; the *dialdehyde*, brown needles, m. p. 186—187°.

Guaiacol ethylene ether, $C_{16}H_{18}O_4$, crystallises in strongly refracting needles, m. p. 139—140°; the *trimethylene ether*, $C_{17}H_{20}O_4$, crystallises in colourless leaflets, m. p. 111°. An aldehyde could not be obtained from either of these ethers. *Vanillin trimethylene ether*, $C_{19}H_{20}O_6$, prepared by the action of sodium ethoxide and trimethylene dibromide on vanillin, crystallises in silvery needles, m. p. 145—146°, and is odourless; the *oxime*, $C_{19}H_{22}O_6N_2$, colourless needles, m. p. 161—162°; the *aniline* derivative, $C_{31}H_{30}O_4N_2$, yellow needles, m. p. 183—184°.

2 : 2′-*Dimethoxydiphenyl*-5 : 5′-*dialdehyde*,

$$CHO{\cdot}C_6H_3(OMe){\cdot}C_6H_3(OMe){\cdot}CHO,$$

prepared from 2 : 2′-dimethoxydiphenyl, crystallises in colourless needles, m. p. 130°. 2 : 2′-*Diethoxydiphenyl*, $C_{16}H_{18}O_2$, prepared by heating *o*-iodophenetole with copper powder, crystallises in colourless leaflets, m. p. 36—37°; the *dialdehyde*, $C_{18}H_{18}O_4$, forms colourless needles, m. p. 128°. G. Y.

Methylation of Vanillin by Methyl Sulphate. HERMAN DECKER and OTTO KOCH (*Ber.*, 1907, 40, 4794—4795).—A simpler and better method of obtaining veratraldehyde than that employed by Perkin and Robinson is described (Trans., 1907, 91, 1079). The method consists in using 0·9 mol. of potassium hydroxide, as the sodium vanillate is sparingly soluble, and gradually adding the alkaline solution to a hot solution of 1 mol. of vanillin and 0·9 mol. of methyl sulphate. The yield is 97%, and the unused vanillin can be recovered. In this method, excess of alkali is avoided, and consequent alteration of the aldehyde prevented. This procedure is applicable to phenols generally. W. R.

Distillation of Calcium Azelate and the Formation of Azelaone. CARL D. HARRIES and LUDWIG TANK (*Ber.*, 1907, 40, 4555—4559).—Working with the products obtained from azelaic acid, the authors show that the substance prepared by the distillation of the calcium salt is not azelaone (*cyclo*octanone), but a complex mixture of isomeric, probably hepta-, hexa-, and penta-cyclic, ketones (compare Derlon, Abstr., 1898, i, 638; Wallach, Abstr., 1907, i, 602). C. S.

Phenyl*iso*crotophenone. HEINRICH WIELAND and HANS STENZL (*Ber.*, 1907, 40, 4825—4833).—*αδ-Dinitro-αδ-diphenyl-Δ^{β}-butylene*, $NO_2{\cdot}CHPh{\cdot}CH{:}CH{\cdot}CHPh{\cdot}NO_2$, is readily formed when a solution of nitric peroxide in pure ether and light petroleum is gradually added to a suspension of diphenylbutadiene in absolute ether surrounded by a freezing mixture. On the addition of light petroleum or ether to its benzene solution, it is deposited in the form of snow-white needles, m. p. 158° (decomp.). When an ethereal suspension of the dinitro-derivative is poured on to dilute aqueous ammonia and repeatedly shaken, nitrous acid is eliminated and *α-nitro-αδ-diphenylbutadiene*, $NO_2\cdot CPh\colon CH\cdot CH\colon CHPh$, is formed. It crystallises from hot alcohol or glacial acetic acid in well-developed, golden-yellow, glistening prisms, m. p. 111—112°, and dissolves in concentrated sulphuric acid to a deep red solution. When reduced with stannous chloride and aqueous alcoholic hydrochloric acid under special conditions, the nitro-derivative yields *phenyl*iso*crotophenone*, $COPh\cdot CH_2\cdot CH\colon CHPh$. This crystallises from hot alcohol in small, colourless needles, m. p. 93°. It does not give a coloration with ferric chloride, and dissolves in concentrated sulphuric acid to a colourless solution. When oxidised with permanganate, it yields benzoic acid. On the addition of sodium hydroxide solution to an alcoholic solution of the ketone, an intensely yellow solution of the sodium derivative of the isomeric enolic compound is formed. The sodium salt can be prepared by the addition of sodium wire to a dry ethereal solution of the ketone, but is readily hydrolysed by water. The corresponding *O-benzoyl* derivative,

$$COPh\cdot O\cdot CPh\colon CH\cdot CH\colon CHPh,$$

forms brilliant, pale yellow crystals, m. p. 128—129°. It gives no reaction with ferric chloride, and is insoluble in cold alkalis, but is readily hydrolysed with warm alkalis.

The *oxime*, $CHPh\colon CH\cdot CH_2\cdot CPh\colon N\cdot OH$, forms colourless crystals, m. p. 104—106°. The ketone readily condenses with benzaldehyde in the presence of piperidine, yielding *dibenzylidenepropiophenone*, $COPh\cdot C(\colon CHPh)\cdot CH\colon CHPh$, in the form of pale yellow needles, m. p. 117°. The ketone also condenses with amyl nitrite and diazobenzene salts. J. J. S.

Direct Hydrogenation of Aromatic Diketones. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1907, **145**, 1126—1127).—The study of the direct hydrogenation of diketones in the presence of nickel (Abstr., 1907, i, 587) has been extended to typical aromatic diketones, and the results show that the reaction proceeds as in the case of the simple aromatic ketones, with formation of the corresponding hydrocarbon (compare Darzens, Abstr., 1905, i, 66). *s*-Diphenylethane (dibenzyl) is obtained by the direct hydrogenation in the presence of nickel of benzil at 220—230°, or of benzoin at 210—220°. When *αγ*-diketo-*α*-phenylbutane (benzoylacetone) is similarly treated at 200°, 80% is converted into butylbenzene, containing traces of the hexahydro-derivative, and the remainder into a mixture of acetone, *iso*propyl alcohol, and toluene. M. A. W.

Morindin. Otto A. Oesterle and Eduard Tisza (*Arch. Pharm.*, 1907, **245**, 534—553. Compare Thorpe and Smith, Trans., 1888, **53**, 171; Perkin and Hummel, Trans., 1894, **65**, 851).—A pyridine solution of morindin when heated with acetic anhydride yields the *acetate*, $C_{27}H_{21}O_6(OAc)_9$, crystallising in thick, light lemon-yellow needles, m. p. 236°. The *benzoate*, $C_{27}H_{21}O_6(OBz)_9$, obtained by the action of benzoyl chloride on morindin in pyridine, crystallises in short, pale yellow needles, m. p. 186°. From the analytical results and the formation of the above derivatives, the authors conclude that morindin has the formula $C_{27}H_{30}O_{15}$, and not $C_{26}H_{28}O_{14}$ as assigned to it by Thorpe. The sugar obtained by the hydrolysis of morindin with dilute sulphuric acid reduces Fehling's solution and ammoniacal silver nitrate solution, has $[\alpha]_D^{20} - 2{\cdot}18°$, and is not fermented by yeast. The presence of a pentose could not be detected. The sugar yields a *phenylosazone*, yellow needles, m. p. 197°, and *a-phenylbenzylhydrazone*, brilliant yellow needles, m. p. 140—141°.

Morindone trimethyl ether, $C_{15}H_7O_2(OMe)_3$, corresponding with the triacetyl derivative described by Perkin and Hummel (*loc. cit.*), results from the action of methyl sulphate on morindone in alkaline solution; it forms a glistening, golden-yellow, fine crystalline powder, m. p. 229°. It is considered probable that morindin has the formula: $OH{\cdot}C_{15}H_7O_2[O{\cdot}C_6H_7O(OH)_4]_2$ or $C_{15}H_7O_2(OH)_2{\cdot}O{\cdot}C_{12}H_{14}O_3(OH)_7$.

W. H. G.

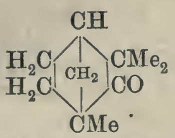
Syntheses of Optically Active *p*-Menthone. ARTHUR KÖTZ and ADOLF SCHWARZ (*Annalen*, 1907, **357**, 209—213).—By a series of transformations, Kötz and Hesse (Abstr., 1906, i, 88) synthesised *d-p*-menthone, starting from a hydroaromatic compound, 1-methyl*cyclo*hexane-3-one. Optically active menthone has now been synthesised from an aliphatic compound, ethyl δ-methyl-*a*-*iso*propylpimelate (this vol., i, 24). This is heated with sodium at 100° and finally at 140°, and the resulting mass is treated with ice-cold dilute sulphuric acid under ether. The ethyl menthonecarboxylate so formed is purified by solution in aqueous sodium carbonate and reprecipitation with sulphuric acid; on distillation, it is obtained as a slightly yellow oil, b. p. 145—149°/14 mm., has a slight odour of peppermint, gives a deep violet coloration with ferric chloride, and on hydrolysis by means of boiling dilute sulphuric acid yields *p*-menthone. *d-p*-Menthone, $[\alpha]_D + 30{\cdot}20°$, is formed also by distilling calcium δ-methyl-*a*-*iso*propylpimelate.

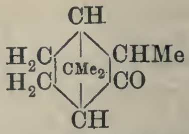
G. Y.

Constituents of Ethereal Oils. I. Separation of Camphor from Fenchone containing Camphor. II. Santene. FRIEDRICH W. SEMMLER (*Ber.*, 1907, **40**, 4591—4598. Compare Abstr., 1907, i, 1062).—The author describes a simple method of separating fenchone from camphor, no convenient method of effecting this separation having hitherto been described.

Fenchone and camphor may be separated by their entirely different behaviour towards sodium, camphor being very readily attacked, whilst fenchone may be distilled from sodium without undergoing decomposition.

This behaviour is adduced in favour of the author's formula for fenchone (I) in preference to Wallach's formula (II):


(I.)


(II.)

The author has also studied santene, C_9H_{14}, obtained by fractionating East Indian sandal-wood oil. The specimen used was optically inactive, had b. p. 31—33°/9 mm., D^{20} 0·863, and n_D 1·46658. The author considers that santene is an unsaturated dicyclic hydrocarbon. When dissolved in benzene and oxidised by ozone, it is converted into the *diketone*, $C_9H_{14}O_2$, b. p. 124—127°/9 mm., D^{20} 1·024, and n_D 1·46658; the *dioxime*, $C_9H_{16}O_2N_2$, has m. p. 129°; the *disemicarbazone*, $C_9H_{14}(:N{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$, has m. p. 216°.

When the ketone, $C_9H_{14}O_2$, is oxidised by sodium hydroxide and bromine, it is converted into the *ketonic acid*, $C_8H_{12}O_3$, which has b. p. 175—205°/9 mm., and forms the *semicarbazone*,

$$C_8H_{12}O_2:N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

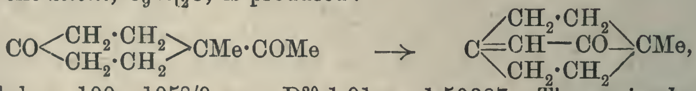
m. p. 168°.

The formation of santene from the tricyclic teresantalic acid, $C_{10}H_{14}O_2$, involves the disruption of the rings; it is not a simple process, but probably takes place in successive phases, as quoted by the author.

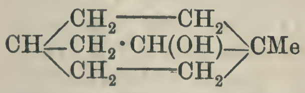
A. McK.

Constituents of Ethereal Oils. Further Derivatives of Santalene and the Formation of a New Dicyclic Saturated System—*dicyclo*-2 : 2 : 2-Octane.

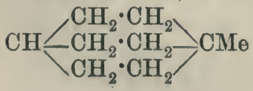
FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1907, 40, 4844—4849. Compare Abstr., 1907, i, 781, and preceding abstract).—When the diketone, $C_9H_{14}O_2$, obtained by oxidising santene with ozone, is boiled for ten minutes with a dilute alcoholic solution of sodium ethoxide, condensation occurs between the methyl group and the ring carbonyl group, and a dicyclic *ketone*, $C_9H_{12}O$, is produced:



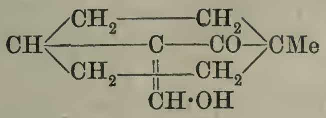
with b. p. 100—105°/9 mm., D^{20} 1·01, n_D 1·50387. The *semicarbazone* has m. p. 205°. When the diketone is reduced with sodium and alcohol, 1-*methyl*dicyclo-2 : 2 : 2-*octane*-7-*ol* is formed, b. p. 98—100°/9 mm., D^{20} 1·001, n_D 1·49668. It is stable towards permanganate. The *acetate*, $C_{11}H_{18}O_2$, has b. p. 104—106°/9 mm., D^{20} 1·011, and n_D 1·47151; the *chloride*, $C_9H_{15}Cl$, has b. p. 82—84°/9 mm., D^{20} 1·019, and n_D 1·49097. When reduced, the chloride yields the corresponding hydrocarbon, 1-*methyl*dicyclo-2:2:2-*octane*, b. p. 149—151°, D^{20} 0·875, and n_D 1·46900.



When oxidised, the alcohol, $C_9H_{16}O$, yields the saturated *ketone*, $C_9H_{14}O$, b. p. 91—94°/9 mm., D^{20} 1·002, n_D 1·48950; the *semicarbazone* of which, $C_{10}H_{17}ON_3$, has m. p.



214°, and the *oxime*, b. p. 132—135°/10 mm., D^{20} 1·051, n_D 1·52058. When reduced, the oxime yields an *amine*, $C_9H_{15}\cdot NH_2$, 7-*amino*-1-*methyl* 2 : 2 : 2-*dicyclooctane*, b. p. 76—77°/9 mm., D^{20} 0·940, n_D 1·49097; the *picrate* has m. p. 206°. The *hydroxymethylene* derivative of the ketone (annexed formula) has b. p. 114—116°/11 mm., D^{20} 1·098, n_D 1·5263, and yields an intense coloration with ferric chloride. J. J. S.



Action of Nitrogen Trioxide on Caoutchouc. Carl D. Harries (*Zeitsch. angew. Chem.*, 1907, **20**, 1969—1970. Compare Abstr., 1905, i, 223).—Polemical. A criticism of Alexander's recent investigations (Abstr., 1907, i, 433). W. H. G.

Lupeol. Pieter van Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, **10**, 292—295; *Compt. rend.*, 1907, **45**, 926—929. Compare Abstr., 1904, i, 905; 1906, i, 20).—Lupeol, obtained from bresk, is not converted into lupeylene under the conditions mentioned by Jungfleisch and Leroux (Abstr., 1907, i, 783). It does not lose water when heated in a tube at 190°, and the acetate and benzoate obtained from fused lupeol are identical with those obtained from lupeol which has not been heated. The behaviour of lupeol on melting has been studied, and it is found that this compound exists in two modifications. W. H. G.

Solubility of "half-hard" African Copals. Charles Coffignier (*Bull. Soc. chim.*, 1907, [iv], **1**, 1131—1143).—The author is making a systematic investigation of the chief analytical constants of the copals of commerce, and has already recorded these for the East African and American resins (Abstr., 1906, i, 870; 1907, i, 67). The present paper gives constants for West African copals.

Benguela copal has D^{16} 1·058, m. p. 165°, acid number 123·1, and Köttstorfer number 157·1. Angola white copal has D^{17} 1·055, m. p. 95°, acid number 127, and Köttstorfer number 159·9. Angola red copal has D^{17} 1·066, m. p. $>300°$, acid number 128·3, and Köttstorfer number 131·8. Congo copal has D^{17} 1·061, m. p. 195°, acid number 132·3, and Köttstorfer number 131·8. Sierra Leone copal has D^{19} 1·072, m. p. 130°, acid number 110·2, and Köttstorfer number 123·4.

The solubilities of these resins, under various conditions, in a number of organic solvents have been determined, and are given in the original. T. A. H.

Alcohols and Resinous Acids in the Varnish from the Leaves of Alnus Glutinosa. Hans Euler and Astrid Euler (*Ber.*, 1907, **40**, 4760—4764).—From the varnish which covers the leaves of *Alnus glutinosa*, the authors have isolated two crystalline saturated alcohols which do not give the cholesterol reaction, and also two amorphous unsaturated resinous acids which give a marked cholesterol reaction.

Glutinol, $C_{14}H_{28}O$, separates from alcohol in leaflets, m. p. 70—71°. *Glutanol*, $C_{14}H_{26}O_2$ (?), m. p. 76°, differs from glutinol in being soluble in ether with difficulty. *Glutinolic acid*, $(C_{28}H_{48}O_5)_x$, softens at 80°, and is possibly a mixture of isomerides. *Glutinic acid*, $C_{28}H_{44}O_7$, also does not melt sharply. A. McK.

Transformation of Barbaloin into an Isomeride, β-Barbaloin; Existence of this Latter in Several Aloes. EUGÈNE LÉGER (*Compt. rend.*, 1907, **145**, 1179—1181. Compare Abstr., 1907, i, 631).—When barbaloin is heated at 160—165° for three hours, it loses its water of crystallisation, and is partially converted into an optical isomeride, *β-barbaloin*, which is obtained as an amorphous residue after the barbaloin has been removed by successive crystallisations of an alcoholic extract of the fused mass. β-Barbaloin yields the *chloro*-derivative, $C_{21}H_{16}O_9Cl_4,5H_2O$, crystallising in prismatic needles, and a *bromo*-derivative, $C_{21}H_{16}O_9Br_4$. A chloride, $C_{21}H_{16}O_9Cl_4,4H_2O$, crystallising in prismatic needles, is obtained by treating with hydrochloric acid and potassium chlorate the mixture obtained by heating barbaloin at 160—165°; this is a mixture of the chlorides of barbaloin and the β-isomeride, and the same mixture is obtained to the extent of 20—22% by the direct chlorination of Cape aloes, whereas they yield only 5% to 6% of crystalline barbaloin; it follows therefore that Cape aloes are richer in aloins than is generally admitted, but that part is present as the amorphous β-barbaloin. Similar results were obtained with Uganda and Socotra aloes. These yielded 20·10% and 23·35% respectively of the chloro-derivative, crystallising in needles, or the β-barbaloin can be isolated from the aloes by evaporating the mother liquors from which the barbaloin has been crystallised.

By the direct chlorination of Cape or Uganda aloes, in addition to the compound mentioned above, a *compound*, $C_{14}H_4O_3Cl_4$, is obtained as yellowish-white needles. This is probably methoxytetrachloronaphthaquinone. M. A. W.

Tannin. MAXIMILIAN NIERENSTEIN (*Ber.*, 1907, **40**, 4575—4576).—Quebracho-tannin is oxidised by potassium persulphate in acetic acid containing a little concentrated sulphuric acid to a dark red substance, *rufiquebrachic acid*, which yields anthracene when distilled with zinc dust. C. S.

Tannic Acid in Toxicological Investigations. PIETRO BIGINELLI (*Gazzetta*, 1907, **37**, ii, 506—520).—When tannic acid is employed as a precipitant for alkaloids, it must be borne in mind that it also forms insoluble compounds with other substances, such as certain solvents and mineral acids. Some of these compounds have been studied by the author.

With ether, tannic acid forms the following *compounds*:

$$C_{14}H_{10}O_9,2Et_2O \text{ and } C_{14}H_{10}O_9,3Et_2O,$$

both of which are converted into the ordinary dihydrate,

$$C_{14}H_{10}O_9,2H_2O,$$

on exposure to the air. When the dihydrate or its aqueous solution is treated with aqueous ether, the syrupy *compound*,

$$C_{14}H_{10}O_9,5Et_2O,6H_2O,$$

is obtained. With alcohol, the *compounds*:

$$C_{14}H_{10}O_9,2EtOH \text{ and } C_{14}H_{10}O_9,3EtOH$$

are formed, whilst chloroform, benzene, and light petroleum form no such compounds on treatment with aqueous 10% tannic acid solution.

With mineral acids, the following *compounds* are formed:

$$C_{14}H_{10}O_9,H_2SO_4,12H_2O;$$

$C_{14}H_{10}O_9,H_2SO_4,14H_2O$, and $3C_{14}H_{10}O_9,2HCl,20H_2O$. The fact that these compounds are precipitated from relatively dilute mineral acid solutions, for example, 5% hydrochloric acid, renders it necessary to employ sufficiently diluted solutions when tannic acid is used as a precipitant for the alkaloids.

The formation of tannates of quinine is also discussed (compare Abstr., 1907, i, 955). T. H. P.

Action of Carbamide, Thiocarbamide, Urethane, and some Amides on Xanthhydrol. ROBERT FOSSE (*Compt. rend.*, 1907, **145**, 813—815).—Xanthhydrol condenses with certain primary amides and with unsubstituted diamides, forming xanthyl amides and dixanthyl diamides respectively, which are very easily split up by the halogen acids, regenerating the amide, and forming unstable xanthyl halide salts. *Dixanthylcarbamide* is probably the symmetrical compound: $CO[NH{\cdot}CH{:}(C_6H_4)_2{:}O]_2$. It forms faintly rose-coloured, silky needles, m. p. varying from 250° to 257—258°, according to the rapidity of heating, which are not altered by boiling aqueous alkali hydroxides. *Dixanthylthiocarbamide*, $CS[NH{\cdot}CH{:}(C_6H_4)_2{:}O]_2$, forms small needles, having m. p. about 200° (decomp.), but varies with the time of heating. *Phenylxanthylthiocarbamide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}CH{:}(C_6H_4)_2{:}O$, crystallises in white, silky needles, which become green at 170°, then melt to a blue liquid, rapidly becoming maroon-coloured. *Xanthylurethane*, $O{:}(C_6H_4)_2{:}CH{\cdot}NH{\cdot}CO_2Et$, forms fine needles, m. p. 168—169°; *xanthylacetamide*, $O{:}(C_6H_4)_2{:}CH{\cdot}NH{\cdot}COMe$, white needles, m. p. 238—244°; *xanthylpropionamide*, $O{:}(C_6H_4)_2{:}CH{\cdot}NH{\cdot}COEt$, colourless needles, m. p. 211—214°; *xanthylbutyramide*, $O{:}(C_6H_4)_2{:}CH{\cdot}NH{\cdot}COPr$, colourless needles, m. p 186—187°; *xanthyl*iso*valeramide*,

$$O{:}(C_6H_4)_2{:}CH{\cdot}NH{\cdot}CH_2{\cdot}CHMe_2,$$

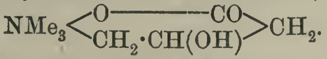
white, silky needles, m. p. 182—184°; *xanthylphenylacetamide*,

$$O{:}(C_6H_4)_2{:}CH{\cdot}NH{\cdot}CO{\cdot}CH_2Ph,$$

silky needles, m. p. 196—197°. E. H.

Extractives of Muscle. IX. Constitution of Carnitine. R. KRIMBERG (*Zeitsch. physiol. Chem.*, 1907, **53**, 514—525. Compare Abstr., 1905, i, 726; 1907, i, 264).—The acid obtained by the decomposition of carnotine appears to be crotonic acid or an isomeride.

When the base is heated with hydriodic acid and red phosphorus at 130° for six hours, it yields a product identical with Willstätter's γ-trimethylbutyrobetaine (Abstr., 1902, i, 268). Carnitine is therefore undoubtedly a hydroxy-derivative of the betaine, probably



$$NMe_3{<}\begin{matrix}O\text{———}CO\\CH_2{\cdot}CH(OH)\end{matrix}{>}CH_2.$$

J. J. S.

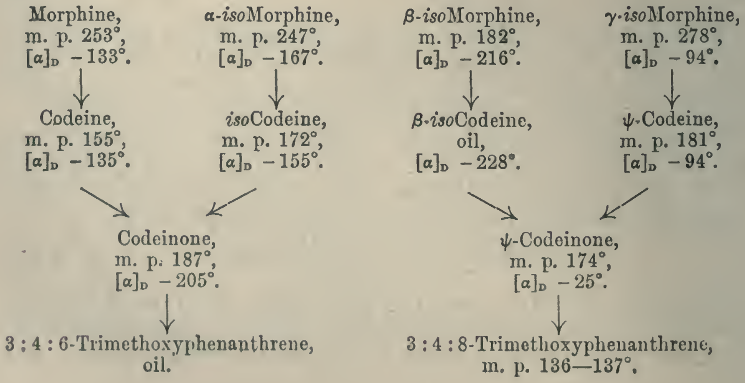
Morphine. XVI. New Chlorocodide. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, **40**, 4883—4889. Compare Abstr., 1907, i, 789, 956).—The β-chloromorphide (Ach and Steinbock, Abstr., 1907, i, 1069), an intermediate product in the formation of *apo*morphine, which is an isomeride of chloromorphide (Schryver and Lees, Trans., 1900, **77**, 1029), yields, when methylated, a new *chlorocodide*; which, since it gives deoxycodeine on reduction, contains the carbon-nitrogen skeleton of morphine. The isomerism between the two chloromorphides or the two chlorocodides is regarded as optical or position isomerism. In confirmation, β-chlorocodide, on hydrolysis, yields other products than the α-isomeride, namely, *iso*codeine (Lees, Proc., 1906, **22**, 253; 1907, **23**, 200; Trans, 1907, **91**, 1408) and allo-ψ-codeine (Abstr., 1907, i, 956; Lees, *loc. cit.*).

β-Chloromorphide has $[\alpha]_D^{15} -5^\circ$ in methyl alcohol. When methylated with diazomethane, it forms *β-chlorocodide*, separating in well-formed, right-angled plates, m. p. 152—153° (the same as α-chlorocodide, but a mixture of the two melted 30° lower); it has $[\alpha]_D^{15} -10^\circ$.

β-Chlorocodide is obtained from codeine or ψ-codeine by heating with fuming hydrogen chloride in sealed tubes at 60—70°, or from α-chlorocodide in a similar manner; it yields deoxycodeine when reduced with zinc dust and alcohol. When hydrolysed by boiling with dilute acetic acid, it yields a product, m. p. 140—150°, $[\alpha]_D^{15} -170^\circ$, which, on crystallisation, proved to be identical with the *A*-base of Lees and Tutin (*loc. cit.*); this Lees (*loc. cit.*) has recognised as a molecular compound of *iso*codeine and β-*iso*codeine. Separation was effected by means of the acid oxalate, and the pure *iso*codeine obtained. E. F. A.

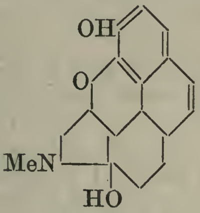
Morphine. XVII. Relationship of *iso*Codeine to Codeine. Ludwig Knorr and Heinrich Hörlein (*Ber.*, 1907, **40**, 4889—4892). —*iso*Codeine, when oxidised with chromic acid in sulphuric acid solution, forms codeinone, identified by means of the oxime. Codeine and *iso*codeine are therefore identical in structure, and only differ with respect to the configuration of the groups attached to the asymmetric carbon atom in position 6.

The genetic relationship of the four isomeric morphines and codeines is therefore established, as shown in the following table (compare Schryver and Lees, Trans., 1901, **79**, 579; Lees and Tutin, Proc., 1906, **22**, 253; Oppé, Abstr., 1907, i, 547; Lees, Proc., 1907, **23**, 200, Trans., 1907, **91**, 1408):

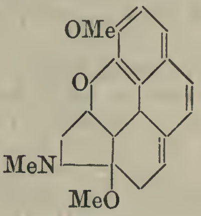

Morphine, m. p. 253°, [α]D −133°.
α-*iso*Morphine, m. p. 247°, [α]D −167°.
β-*iso*Morphine, m. p. 182°, [α]D −216°.
γ-*iso*Morphine, m. p. 278°, [α]D −94°.
Codeine, m. p. 155°, [α]D −135°.
*iso*Codeine, m. p. 172°, [α]D −155°.
β-*iso*Codeine, oil, [α]D −228°.
ψ-Codeine, m. p. 181°, [α]D −94°.
Codeinone, m. p. 187°, [α]D −205°.
ψ-Codeinone, m. p. 174°, [α]D −25°.
3 : 4 : 6-Trimethoxyphenanthrene, oil.
3 : 4 : 8-Trimethoxyphenanthrene, m. p. 136—137°.

These facts are discussed in relation to the bridged-ring formula proposed for morphine (see Abstr., 1907, i, 789), according to which it contains four asymmetric carbon atoms. The configuration of three of these (positions 5, 9, and 13) is fixed by the bridge. But two optically active isomerides corresponding with position 6 are therefore possible. These are represented by morphine and *iso*morphine, and by their methyl ethers, codeine and *iso*codeine. The *β*- and *γ*-*iso*morphines and their methyl ethers differ from the above bases in the position of the alcohol hydroxyl group; in these, attached to position 8. In the ketones, codeinone and *ψ*-codeinone, the structural isomerism is due to the same difference in the position of the keto-group. E. F. A.

Constitution of Morphine and Thebaine. Hans Th. Bucherer (*J. pr. Chem.*, 1907, [ii], 76, 428—432).—The results obtained in the investigation of the action of sulphites on pyridine and its derivatives, and consequently on morphine and thebaine, which will be published in detail later, have led the author to suggest for these two alkaloids the following structural formulæ, which are discussed shortly:



Morphine.

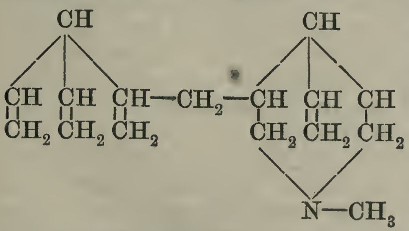


Thebaine.

G. Y.

Sparteine. Application of Hofmann's Reaction to Sparteine Methylhemisparteilene. Charles Moureu and Amand Valeur (*Compt. rend.*, 1907, **145**, 815—817. Compare Abstr., 1905, i, 716).—Crude methylsparteine (α_D −25·2° in alcohol), obtained by distilling methylsparteinium hydroxide in a vacuum, when treated with methyl iodide is methylated to the extent of 66%. From the methiodide formed, crude dimethylsparteine (α_D +0·61°) is obtained, which on treatment with excess of methyl iodide gives a *dimethiodide*, $C_{15}H_{24}Me_2N_2,2MeI,H_2O$. The latter by the action of moist silver oxide (2 mols.) gives *tetramethylsparteinium dihydroxide*, $C_{15}H_{24}Me_2N_2(MeOH)_2$, which on distillation gives *methylhemisparteilene*, $C_{16}H_{25}N$, a liquid, b. p. 160—161°/16 mm., and α_D + 156·5° (in alcoholic solution).

From its mode of formation, methylhemisparteilene should contain methyl attached to nitrogen, and four ethylenic linkings. These deductions are confirmed by analysis and by the molecular refractive power respectively. Thus the degradation of sparteine by Hofmann's reaction is more



profound than was at first considered, involving five instead of three piperidine nuclei. Only one of the latter remains in methylhemisparteilene. E. H.

Two Isomeric Methylsparteines. Charles Moureu and Amand Valeur (*Compt. rend.*, 1907, **145**, 929—930).—The crude methylsparteine, obtained by decomposing α-methylsparteinium hydroxide (preceding abstract), has $\alpha_D - 25°$, and is a mixture of 10% of sparteine and 90% of α- and β-methylsparteine. The three bases can be separated by warming the mixture with a slight excess of normal sulphuric acid, whereby the α-methylsparteine sulphate is converted into the methosulphate; the sparteine and β-methylsparteine sulphates do not undergo this isomeric change, and the bases are separated by fractional crystallisation of the hydriodides.

α-Methylsparteine, $C_{15}H_{25}N_2Me$, m. p. 30—31°, b. p. 178—179° (corr.)/11 mm., has a faint odour, and has $\alpha_D - 55{\cdot}4°$ in absolute alcoholic solution. The *dihydrochloride* is very deliquescent; the *platinichloride*, $C_{15}H_{25}N_2Me,H_2PtCl_6,3H_2O$, is microcrystalline, and decomposes at 247°; the *dihydriodide*, $C_{15}H_{25}N_2Me,2HI$, crystallises in needles, and has $\alpha_D - 38{\cdot}3°$, and the *picrate*, $C_{15}H_{25}N_2Me,C_6H_3O_7N_3$, is amorphous.

β-Methylsparteine, $C_{15}H_{25}N_2Me$, a colourless liquid, b. p. 181—183° (corr.)/16·5 mm., $\alpha_D + 9{\cdot}9°$, has an odour of onions, and is less stable in air than its isomeride. The *hydriodide*, $C_{15}H_{25}N_2Me,HI,2H_2O$, is crystalline; the anhydrous salt has m. p. 77—78°, and $\alpha_D - 32{\cdot}2°$ in aqueous, or $- 28{\cdot}2°$ in methyl-alcoholic, solution; the *dihydriodide*, $C_{15}H_{25}N_2Me,2HI$, is crystalline, and has $\alpha_D - 13{\cdot}5°$ in methyl-alcoholic solution; the *platinichloride*, $C_{15}H_{25}N_2Me,H_2PtCl_6,3H_2O$, has m. p. 230°, and the *picrate*, $C_{15}H_{25}N_2Me,2C_6H_3O_7N_3$, has m. p. 94—95°.

α- and β-Methylsparteines are unsaturated bases, and in each compound the methyl group is attached to a nitrogen atom (compare Herzig and Meyer, Abstr., 1896, i, 68). M. A. W.

Sparteine. Isomerisation of α-Methylsparteine. Charles Moureu and Amand Valeur (*Compt. rend.*, 1907, **145**, 1184—1185. Compare preceding abstracts).—When α-methylsparteine dihydriodide, $C_{15}H_{25}N_2Me,2HI$, is heated in a sealed tube at 125° with twice its weight of water, it is partially converted into iso*sparteine methiodide*, $C_{15}H_{26}N_2,MeI$, $\alpha_D - 16{\cdot}8°$. The same compound is also obtained by treating α-methylsparteine dihydriodide with alkalis, but the yield is poor, and the best results are obtained by heating α-methylsparteine on the water-bath with a slight excess of *N*-sulphuric acid until the solution no longer reduces permanganate solution. The solution is then neutralised with barium hydroxide solution, and, on the addition of barium iodide, the *hydriodide* of iso*sparteine methiodide*,

$$C_{15}H_{26}N_2,MeI_3HI,H_2O,$$

separates. iso*Sparteine hydriodide*, $C_{15}H_{26}N_2,HI$, is obtained in a crystalline form by heating the hydriodide of *iso*sparteine methiodide at 220—225°, and extracting the residue with hot water; it is also obtained by heating, at 225—230°, α-methylsparteine dihydriodide.

M. A. W.

Xanthine Bases. ERNST SCHMIDT (*Arch. Pharm.*, 1907, **245**, 389—398).—In addition to the alkyltheobromines obtained from potassiotheobromine and alkyl iodides (which melt at a lower temperature and are more soluble in water than theobromine itself, in proportion, as the alkyl group contains more carbon atoms), corresponding alkyltheobromines with comparatively high melting points have been described as formed in a similar manner from silver theobromine. It is now shown that the ethyltheobromine of high melting point is really regenerated theobromine; a little ethyltheobromine is formed, but it has the lower melting point. Silver theobromine thus does not react with ethyl iodide to form an alkyl derivative by any means so readily as with methyl iodide. C. F. B.

ψ-Theobromine. ERNST SCHMIDT and WILLMAR SCHWABE, jun. (*Arch. Pharm.*, 1907, **245**, 398—405. Compare Pommerehne, Abstr., 1897, i, 129; 1898, i, 539).—ψ-Theobromine is best prepared by heating silver xanthine with methyl sulphate at 150°; by taking suitable precautions, a yield can be obtained equal to 35—40% of the xanthine employed. The *sulphate*, $B,H_2SO_4,2H_2O$; *aurichloride*, $B,HAuCl_4$, m. p. 251°, and *platinichloride*, $2B,H_2PtCl_6,4H_2O$, are described [$B = C_7H_8O_2N_4$]. When ψ-theobromine is boiled with potassium dichromate and dilute sulphuric acid, it is oxidised to methylparabanic acid, methylamine, ammonia, and carbon dioxide; hence, it can only contain one methyl group in the carbamide residue. C. F. B.

Some Alkyl Derivatives of Theophylline. WILLMAR SCHWABE, jun. (*Arch. Pharm.*, 1907, **245**, 312—325. Compare Abstr., 1907, i, 449).—Ethyltheophylline, $C_9H_{12}O_2N_4$, was prepared by boiling dry potassiotheophylline with ethyl iodide and a little ethyl alcohol for six hours, or by digesting the same substance with ethyl sulphate for three days at the ordinary temperature; from it were prepared crystalline salts of the following composition: $B,HCl,2H_2O$ ($2H_2O + HCl$ lost at 100°); B,HBr (stable at 100°); B,H_2SO_4; $B,HAuCl_4$, m. p. 224°; $2B,H_2PtCl_6$; $B,HgCl_2$; $B,Hg(CN)_2$; $B,AgNO_3,H_2O$; B,MeI, 182°; $[B,Me]AuCl_4$, 190°; $[B,Me]_2PtCl_6$, 250°. When ethyltheophylline is added to bromine, *bromoethyltheophylline*, $C_9H_{11}O_2N_4Br$, m. p. 170°, is formed, and, when this is boiled with alcoholic potassium hydroxide, it is converted into *ethoxyethyltheophylline*, $C_{11}H_{16}O_3N_4$, m. p. 78°. When ethyltheophylline is boiled with potassium dichromate and dilute sulphuric acid, it yields dimethylparabanic acid (cholestrophan), $C_5H_6O_2N_3$, m. p. 151° (not 145°, as stated usually), ethylamine, ammonia, and carbon dioxide. Ethyltheophylline is to be regarded as a 1 : 3-dimethyl-7-ethyl derivative.

n-Propyltheophylline, $C_{10}H_{14}O_2N_4$, was obtained by heating potassiotheophylline with *n*-propyl iodide and a little alcohol in a sealed tube in the water-bath. Salts: *aurichloride*, $B,HAuCl_4,2H_2O$, m. p. 214°; *platinichloride*, $2B,H_2PtCl_6,2H_2O$, crystalline.

iso*Propyltheophylline* was prepared by heating potassiotheophylline with *iso*propyl iodide and a little alcohol at 150°. Salts: *aurichloride*, $B,HAuCl_4,H_2O$, m. p. 183°; *platinichloride*, $2B,H_2PtCl_6,2H_2O$, m. p. (anhydrous) 201°.

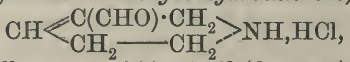
Benzyltheophylline, $C_{14}H_{14}O_2N_4$, was obtained by heating potassiotheophylline with benzyl chloride in a sealed tube in the water-bath. The *aurichloride*, $B,HAuCl_4$, m. p. 104°, and *platinichloride*,

$$2B,H_2PtCl_6,$$

crystalline, are only stable in the presence of excess of the corresponding acids; they are decomposed by water with separation of benzyltheophylline. C. F. B.

Aminoacetals and Aminoaldehydes. ALFRED WOHL (*Ber.*, 1907, 40, 4679—4684).—A discussion of the results contained in the following five abstracts and this vol., i, 17. W. H. G.

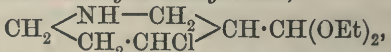
Tetrahydropyridine-3-aldehyde and Piperidine-3-aldehyde. ALFRED WOHL and M. S. LOSANITSCH, jun. (*Ber.*, 1907, 40, 4685—4698).—β-Iminodipropaldehyde tetraethylacetal (compare Abstr., 1906, i, 106) is converted by concentrated hydrochloric acid into Δ^3-*tetrahydropyridine-3-aldehyde hydrochloride*,



$$\mathrm{CH}{<}\begin{matrix}\mathrm{C(CHO)\cdot CH_2}\\ \mathrm{CH_2\text{——}CH_2}\end{matrix}{>}\mathrm{NH,HCl},$$

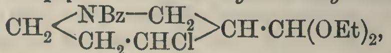
crystallising in needles, m. p. 144—145° (decomp.). The *free aldehyde*, C_6H_9ON, cannot be prepared from the hydrochloride by the action of potassium carbonate or sodium ethoxide, but is obtained in a polymerised form by dissolving the hydrochloride in cold diethylamine; it is a pale yellow, amorphous substance. The *oxime hydrochloride*, $C_6H_{10}ON_2,HCl$, forms colourless crystals, decomposing at 252° (corr.); treatment with potassium carbonate liberates the free *oxime*, $C_6H_{10}ON_2$; it forms groups of colourless crystals, softens at 142°, m. p. 144·5—145·5° (corr.).

4-*Chloropiperidine-3-aldehyde diethylacetal*,



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{NH\text{—}CH_2}\\ \mathrm{CH_2\cdot CHCl}\end{matrix}{>}\mathrm{CH\cdot CH(OEt)_2},$$

prepared by the action of hydrogen chloride on the hydrochloride of Δ^3-tetrahydropyridine-3-aldehyde dissolved in ethyl alcohol, is a colourless oil, b. p. 74°/0·15 mm. It readily loses hydrogen chloride, and consequently, on hydrolysis, is converted, not into the chloroaldehyde, but into Δ^3-tetrahydropyridine-3-aldehyde hydrochloride. It is converted on treatment with benzoyl chloride and sodium hydroxide into 1-*benzoyl*-4-*chloropiperidine-3-aldehyde diethylacetal*,



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{NBz\text{—}CH_2}\\ \mathrm{CH_2\cdot CHCl}\end{matrix}{>}\mathrm{CH\cdot CH(OEt)_2},$$

obtained as a soft, pale yellow mass, m. p. 35—40°. It does not give off hydrogen chloride so readily as the parent substance.

4-*Chloropiperidine-3-aldehyde dimethylacetal*, $C_8H_{16}O_2NCl$, is a colourless oil, b. p. 68—69°/0·15 mm.

1-*Benzoyl*-Δ^3-*tetrahydropyridine-3-aldehyde*, $C_{13}H_{13}O_2N$, prepared by acting on β-iminodipropaldehyde tetraethylacetal in pyridine with benzoyl chloride and treating the product so formed with concentrated hydrochloric acid, forms colourless crystals, m. p. 90·5—91·5° (corr.). The corresponding m-*nitrobenzoyl* derivative, prepared in a similar manner, crystallises in colourless prisms, sinters at 160°, m. p.

161—162° (corr.). An acetal derivative of this compound could not be prepared.

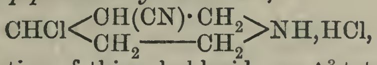
4-Chloropiperidine-3-aldehyde diethylacetal is reduced by sodium and ethyl alcohol to *piperidine-3-aldehyde diethylacetal*, $C_{10}H_{21}O_2N$, a colourless liquid, b. p. 55°/0·15 mm., 104·5—105°/8·5 mm. It is hydrolysed by concentrated hydrochloric acid with the production of *piperidine-3-aldehyde hydrochloride*, but, since this could not be obtained in a crystalline form, the *platinichloride*,

$$C_{12}H_{22}O_2N_2,H_2PtCl_6,$$

orange needles or rhombohedra, decomposing at 168—178°, and the m-*nitrophenylhydrazone hydrochloride*, $C_{12}H_{16}O_2N_4,HCl$, golden-yellow crystals, decomposing at 232—233° (corr.), were prepared. Piperidine-3-aldehyde hydrochloride, on treatment with diethylamine, yields the free *piperidine-3-aldehyde*, but, as is shown by mol. wt. determinations, only in the bimolecular form, $(C_6H_{11}ON)_2$; it is obtained as a pale yellow, amorphous mass. W. H. G.

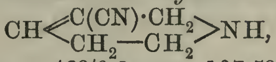
Synthesis of the Racemic Cincholeuponic Acids. Alfred Wohl and M. S. Losanitsch, jun. (*Ber.*, 1907, 40, 4698—4711).—Two stereoisomeric 4-pipecoline-3 : ω-dicarboxylic acids, representing the two racemic forms of the cincholeuponic acids (compare Königs, Abstr., 1896, i, 264; 1897, i, 497), have been synthesised from β-iminodipropaldehyde tetraethylacetal by way of Δ^3-tetrahydropyridine-3-aldoxime (compare preceding abstract) and 3-cyano-Δ^3-tetrahydropyridine. The acid, m. p. 211°, is named α- and the other acid, m. p. 229°, is named β-*r*-cincholeuponic acid; they have not yet been resolved into the active forms.

4-*Chloro-3-cyanopiperidine hydrochloride*,



$$\mathrm{CHCl}\!<\!\begin{array}{l}\mathrm{CH(CN)\cdot CH_2}\\ \mathrm{CH_2{-\!\!-\!\!-}CH_2}\end{array}\!>\!\mathrm{NH,HCl},$$

obtained by the action of thionyl chloride on Δ^3-tetrahydropyridine-3-aldoxime hydrochloride, crystallises in colourless plates and long, blunt prisms, decomposing at 192—193° (corr.). It is converted by sodium hydroxide in aqueous solution into 3-*cyano-Δ^3-tetrahydropyridine*,



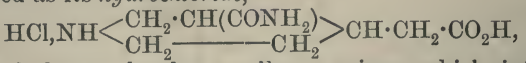
$$\mathrm{CH}\!<\!\begin{array}{l}\mathrm{C(CN)\cdot CH_2}\\ \mathrm{CH_2{-}CH_2}\end{array}\!>\!\mathrm{NH},$$

a colourless liquid, b. p. 48°/0·2 mm., 107·5°/12 mm.; the *platinichloride*, $C_{12}H_{16}N_4,H_2PtCl_6$, crystallises in long, golden-yellow needles, decomposing at 208—209° (corr.). Δ^3-*Tetrahydropyridine-3-carboxylic acid hydrochloride*, $C_6H_9O_2N,HCl$, is prepared by treating 4-chloro-3-cyanopiperidine hydrochloride successively with concentrated hydrochloric acid, barium hydroxide, and sulphuric acid; it crystallises in colourless prisms and needles, decomposing at 309—314° (corr.); the *platinichloride*, $(C_6H_9O_2N)_2,H_2PtCl_6$, crystallises in golden-yellow needles, decomposing at 215—224° (corr.); the *aurichloride*,

$$C_6H_9O_2N,HAuCl_4,$$

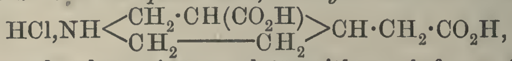
forms lemon-yellow prisms, m. p. 190° (decomp.); heated quickly, m. p. 196° (decomp.).

3-Cyano-Δ^3-tetrahydropyridine condenses with ethyl malonate in the presence of sodium ethoxide in alcoholic solution with the formation of a "crude product," which, when heated for a short time with barium hydroxide and water, yields *α-r-3-carboxylamido-4-piperidylacetic acid*, obtained as its *hydrochloride*,



$$\mathrm{HCl,NH}<\begin{matrix}\mathrm{CH_2\cdot CH(CONH_2)}\\ \mathrm{CH_2 \text{———} CH_2}\end{matrix}>\mathrm{CH\cdot CH_2\cdot CO_2H},$$

crystallising in long, colourless needles or prisms, which sinter at 242° and decompose at 244—245° (corr.); heated quickly, at 251° (corr.). It is converted by concentrated hydrochloric acid into *α-r-cincholeuponic acid hydrochloride*. α-r-3-*Cyano-4-piperidylacetic acid* results on heating the above "crude product" for one to one and a-half hours with barium hydroxide and water; the *hydrochloride*, $C_8H_{12}O_2N_2,HCl$, forms long, spear-shaped, colourless crystals, decomposing at 330° (corr.); it yields *α-r*-cincholeuponic acid when hydrolysed with concentrated hydrochloric acid. The "crude product," when heated from six to twelve hours with barium hydroxide and water, is converted almost entirely into α-r-*cincholeuponic acid*, the *hydrochloride* of which,



$$\mathrm{HCl,NH}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2 \text{———} CH_2}\end{matrix}>\mathrm{CH\cdot CH_2\cdot CO_2H},$$

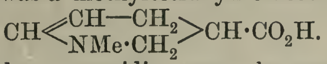
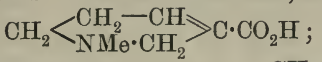
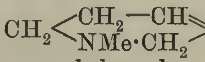
crystallises in colourless prisms or plates with rough faces; it softens at 210°, decomposes at 212—213° (corr.). The free *acid* is obtained from the hydrochloride by treating it with slight excess of silver carbonate; it crystallises with 1 mol. of water in large, colourless prisms, decomposing at 145°; the *anhydrous* acid decomposes at 208—209°. The *hydrobromide*, $C_8H_{13}O_4N,HBr$, crystallises in prisms, softens at 218°, m. p. 224—225° (decomp.); the hydrated *platinichloride*,

$$C_{16}H_{26}O_8N_2,H_2PtCl_6,2H_2O,$$

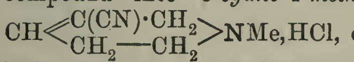
crystallises in orange-coloured plates or flat prisms, decomposing at 160—170°; the *anhydrous*, golden-yellow salt sinters at 205° and decomposes at 210° (corr.). A cold aqueous solution of *α-r*-cincholeuponic acid hydrochloride, when treated with sodium nitrite, yields 1-*nitroso*-α-r-*cincholeuponic acid*, $C_8H_{12}O_5N_2$, crystallising in almost colourless prisms, m. p. 152—153° (decomp. corr.). *α-r*-Cincholeuponic acid is decomposed by concentrated sulphuric acid at 270—280° with the formation of 4-methylpyridine (compare Skraup, Abstr., 1897, i, 98), the platinichloride of which does not melt at 237° as given by Skraup, but decomposes at 244—245°; heated rapidly, at 258° (corr.).

β-r-*Cincholeuponic acid hydrochloride* is the chief product resulting from the action of concentrated hydrochloric acid on the above "crude product"; it crystallises in flat prisms, decomposing at 223—224° (corr.), or, when heated quickly, at 229°. When heated with potassium hydroxide solution for six hours at 180—190°, it is converted into the α-acid. *β*-r-*Cincholeuponic acid*, $C_8H_{13}O_4N$, crystallises in colourless prisms, decomposing at 248—249° (corr.); heated slowly, at 242° (corr.); the *hydrobromide*, $C_8H_{13}O_4N,HBr$, forms large, granular crystals, decomposing at 226° (corr.); the *platinichloride*, $C_{16}H_{26}O_8N_2,H_2PtCl_6,2H_2O$, crystallises in orange-coloured, rhombic plates or prisms, decomposing at 218—225° (corr.). 1-*Nitroso*-*β*-r-*cincholeuponic acid*, $C_8H_{12}O_5N_2$, is not so stable as the α-compound; it softens at 156°, m. p. 157—158° (decomp.). The *β*-acid is converted under the same conditions as the α-acid into 4-methylpyridine.

W. H. G.

Arecaidine and Arecoline. Alfred Wohl and A. Johnson (*Ber.*, 1907, 40, 4712—4719. Compare preceding abstract).—Arecaidine was first synthesised by Jahns (Abstr., 1892, 737), who showed that it was a methyltetrahydronicotinic acid and assigned to it the formula:  $CH<\substack{CH—CH_2\\ NMe\cdot CH_2}>CH\cdot CO_2H$. The authors show in the present paper how arecaidine may be synthesised from β-methyliminodipropaldehyde tetraethylacetal by way of 1-methyl-Δ^3-tetrahydropyridine-3-aldehyde and 3-cyano-1-methyl-Δ^3-tetrahydropyridine. From its mode of formation, it follows that the position of the ethylene-linking in Jahns' formula is incorrect, and that arecaidine has the constitution:  $CH_2<\substack{CH_2—CH\\ NMe\cdot CH_2}>C\cdot CO_2H$; arecoline must consequently be represented by the formula:  $CH_2<\substack{CH_2—CH\\ NMe\cdot CH_2}>C\cdot CO_2Me$.

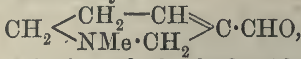
β-Methyliminodipropaldehyde tetraethylacetal, $NMe[CH_2\cdot CH_2\cdot CH(OEt)_2]_2$, is prepared by heating under pressure a benzene solution of methylamine (three mols.) and β-chloropropaldehyde acetal (two mols.) at 125—135°; it is an almost colourless oil, b. p. 112°/0·48 mm. At the same time is formed small quantities of *β-methylaminopropaldehyde diethylacetal*, $NHMe\cdot CH_2\cdot CH_2\cdot CH(OEt)_2$, a colourless oil.

1-*Methyl-Δ^3-tetrahydropyridine*-3-*aldehyde hydrochloride*, $C_7H_{11}ON,HCl$, results on treating the above tertiary base with cold concentrated hydrochloric acid; it forms long, white crystals, m. p. 194·5° (corr.). The *oxime hydrochloride*, $C_7H_{12}ON_2,HCl$, crystallises in long, colourless needles, m. p. 249·5° (corr.). Thionyl chloride converts the latter compound into 3-*cyano*-1-*methyl-Δ^3-tetrahydropyridine hydrochloride*,  $CH<\substack{C(CN)\cdot CH_2\\ CH_2—CH_2}>NMe,HCl$, colourless needles, m. p. 230·5° (corr.). This substance on hydrolysis with concentrated hydrochloric acid yields arecaidine (1-methyl-Δ^3-tetrahydronicotinic acid) hydrochloride, identical in all respects with that obtained from the betel-nut; the platinichloride, heated quickly, gives m. p. 225—226° (corr.); Jahns (*loc. cit.*) gives m. p. 208—209°. The arecoline prepared by the methylation of arecaidine, obtained as above, yields a methiodide identical with that described by Willstätter (Abstr., 1897, i, 385). *Arecoline hydrobromide*, $C_8H_{13}O_2N,HBr$, crystallises in slender prisms, m. p. 167—169° (corr.); the *hydrochloride* forms deliquescent, slender needles, m. p. 157—158° (corr.). W. H. G.

A Tertiary Triacetal Base and Arecaidinealdehyde. Alfred Wohl and E. Grosse (*Ber.*, 1907, 40, 4719—4722. Compare preceding abstract).—An investigation on tripropaldehydehexaethylacetalamine, $N[CH_2\cdot CH_2\cdot CH(OEt)_2]_3$; the chemical properties of such tertiary triacetal bases have not hitherto been studied.

Tripropaldehydehexaethylacetalamine is formed together with β-iminodipropaldehyde tetraethylacetal by the action of ammonia on β-chloropropaldehyde diethylacetal (compare Wohl, Hertzberg, and Losanitsch, Abstr., 1906, i, 106). It is a lemon-yellow, viscid oil,

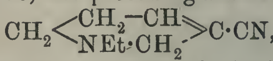
b. p. 209—210°/11 mm., 127—128°/0·06 mm., and combines with methyl iodide, yielding *tripropaldehydehexaethylacetal-methylammonium iodide*, $NMeI[CH_2\cdot CH_2\cdot CH(OEt)_2]_3$, colourless crystals, m. p. 93·5°. An aqueous solution of this compound, treated with silver chloride, yields the corresponding *chloride*, an exceedingly deliquescent substance; the *aurichloride*, $C_{22}H_{47}O_6N,HAuCl_4$, m. p. 57°, is difficultly soluble in water. The chloride, when evaporated with dilute hydrochloric acid in a vacuum at 50°, is decomposed into 1-methyl-Δ^3-tetrahydropyridine-3-aldehyde (arecaidinealdehyde) hydrochloride (compare preceding abstract) and acraldehyde.

Arecaidinealdehyde,  $CH_2{<}\substack{CH_2—CH\\ NMe\cdot CH_2}{>}C\cdot CHO$, may be obtained by acting on an aqueous solution of the hydrochloride with potassium carbonate; it is a colourless oil, b. p. 40—43°/0·17 mm., with a pungent, basic odour, and changes into a dark brown solid when kept a short time. It combines readily with benzoyl chloride, forming *tripropaldehydehexaethylacetal-benzoylammonium chloride*,

$$NBzCl[CH_2\cdot CH_2\cdot CH(OEt)_2]_3,$$

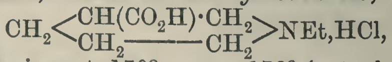
a green, crystalline substance, m. p. 60°. W. H. G.

1-Ethylnipecotinic Acid and ω-Amino-1-ethyl-β-pipecoline.

ALFRED WOHL and M. S. LOSANITSCH, jun. (*Ber.*, 1907, 40, 4723—4727. Compare Abstr., 1906, i, 106, and preceding abstracts). —3-*Cyano*-1-*ethyl*-Δ^3-*tetrahydropyridine*,  $CH_2{<}\substack{CH_2—CH\\ NEt\cdot CH_2}{>}C\cdot CN$, is obtained from its hydrochloride (compare Abstr., 1906, i, 106) on treatment with potassium carbonate; it is a colourless oil, b. p. 51—53°/0·04 mm.; the crystalline *aurichloride*, $C_8H_{12}N_2,HAuCl_4$, m. p. 144—145° (decomp.), decomposes slightly at 110°. The nitrile yields, on hydrolysis with concentrated hydrochloric acid, 1-*ethyl*-Δ^3-*tetrahydropyridine*-3-*carboxylic acid hydrochloride*, $C_8H_{13}O_2N,HCl$, crystallising in white needles, which soften at about 225°, m. p. 232—233° (decomp.); the *platinichloride*, $C_{16}H_{26}O_4N_2,H_2PtCl_6$, decomposes at 229° (corr.) when heated rapidly; the *aurichloride*,

$$C_8H_{13}O_2N,HAuCl_4,$$

crystallises in short, lemon-yellow prisms, softens at about 205°, m. p. 214—215° (corr.). The above tetrahydro-acid hydrochloride is reduced by sodium and ethyl alcohol to 1-*ethylnipecotinic* (1-*ethylpiperidine*-3-*carboxylic*) *acid*, obtained as the *hydrochloride*,



$$CH_2{<}\substack{CH(CO_2H)\cdot CH_2\\ CH_2——CH_2}{>}NEt,HCl,$$

white needles, softening at 170°, m. p. 178° (not sharp); the *aurichloride* crystallises in prisms, m. p. 158° (corr.); the *platinichloride* forms crystals, m. p. 214—215° (decomp.).

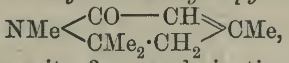
ω-Amino-1-*ethyl-β-pipecoline* (3-*aminomethyl*-1-*ethylpiperidine*) is obtained by the reduction of 1-ethyl-Δ^3-tetrahydropyridine-3-aldoxime with sodium and ethyl alcohol; it is a colourless liquid, b. p. 105—110°/20 mm. The crystalline *aurichloride*,

$$C_8H_{18}N_2,2HAuCl_4,H_2O,$$

m. p. 184—185° (corr.), and *platinichloride*, $C_8H_{18}N_2,H_2PtCl_6.H_2O$, crystallising in orange plates and prisms, m. p. 239° (corr.), were prepared. W. H. G.

Hydrolysis of Oxyhydropyridine Nitriles. I. Galeazzo Piccinini (*Atti R. Accad. Sci. Torino*, 1907, 42, 1004—1017).—The monocarboxylic acids corresponding with 3-cyano-2-keto-4 : 6 : 6-trimethyl-Δ^3-tetrahydropyridine and 3-cyano-2-keto-1 : 4 : 6 : 6-tetramethyl-Δ^3-tetrahydropyridine are unstable, so that, when these cyano-derivatives are hydrolysed, compounds are obtained in which the cyanogen group is replaced by hydrogen.

2-*Keto*-1 : 4 : 6 : 6-*tetramethyl*-Δ^3-*tetrahydropyridine*,



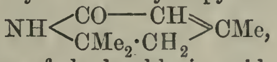
$$\mathrm{NMe}\left<\begin{matrix}\mathrm{CO}\text{—}\mathrm{CH}\\ \mathrm{CMe_2{\cdot}CH_2}\end{matrix}\right>\mathrm{CMe},$$

prepared by hydrolysing its 3-cyano-derivative by the action of an excess of concentrated hydrochloric acid at 140—150°, solidifies in somewhat hygroscopic, hard, colourless crystals, m. p. 49·5°, b. p. 250°/745 mm.; has the normal molecular weight in freezing benzene, and reduces permanganate in the cold. Its *platinichloride*,

$$(C_9H_{15}ON)_2,H_2PtCl_6,$$

m. p. 205·5°, *picrate*, $C_9H_{15}ON,C_6H_3O_7N_3$, m. p. 126°, and *aurichloride*, $(C_9H_{15}ON)_2,HAuCl_4$, m. p. 122—123°, were prepared.

2-Keto-4 : 6 : 6-trimethyl-Δ^3-tetrahydropyridine,



$$\mathrm{NH}\left<\begin{matrix}\mathrm{CO}\text{—}\mathrm{CH}\\ \mathrm{CMe_2{\cdot}CH_2}\end{matrix}\right>\mathrm{CMe},$$

obtained by the action of hydrochloric acid on the corresponding 3-cyano-compound, separates in white crystals, m. p. 120—121° [Benedicenti and Quenda (*R. Acc. Med. Torino*, 51, iv) gave m. p. 115—116°]. Its *hydrochloride*, $C_8H_{13}ON,HCl,H_2O$, m. p. 79—80°, or, in the anhydrous condition, 110—115°, *picrate*, $C_8H_{13}ON,C_6H_3O_7N_3$, m. p. 123°, and *platinichloride*, $(C_8H_{13}ON)_2,H_2PtCl_6,2H_2O$, m. p. 118—120°, or, in the anhydrous state, 177°, were prepared.

T. H. P.

Condensation of γ-Picoline with *o*-Nitrobenzaldehyde. Martin Löwensohn (*Ber.*, 1907, 40, 4860—4863).—γ-Picoline (4-methylpyridine) and *o*-nitrobenzaldehyde condense when heated with zinc chloride under pressure at 170—180° for nine to ten hours, yielding 2′-*nitro*-4-*stilbazole*, $C_{13}H_{10}O_2N_2$, m. p. 98—100°. The *hydrochloride*, $C_{13}H_{10}O_2N_2,HCl$, has m. p. 191—192°; the *nitrate*, m. p. 95°; the *sulphate*, $C_{13}H_{10}O_2N_2,H_2SO_4$, m. p. 110°; the *platinichloride*, m. p. 206°; the *aurichloride*, m. p. 215°; the *mercurichloride*,

$$C_{13}H_{10}O_2N_2,HCl,HgCl_2,$$

m. p. 175—176°, and the *picrate*, m. p. 198°.

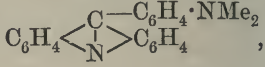
2′-*Amino*-4-*stilbazole*, $C_{13}H_{12}N_2$, immediately forms the carbonate, $(C_{13}H_{12}N_2)_2H_2CO_3$, m. p. 76°. The *hydrochloride* has m. p. 205°; the *sulphate*, m. p. 140°; the *stannichloride*, m. p. 155°, and the *platinichloride*, m. p. 238°.

When reduced with hydriodic acid and red phosphorus at 150°, the amine yields 2′-*aminodihydro*-4-*stilbazole*, $C_{13}H_{14}N_2$, in the form of small, colourless needles, m. p. 76°. The *hydrochloride* has m. p. 247°, and the *picrate* melts above 300°.

The diazo-salts obtained from 2′-amino-4-stilbazole couple with alkaline solutions of phenols, yielding dyes. *4-Stilbazole-2′-azo-β-naphthol hydrochloride*, $C_{23}H_{14}ON_3Cl$, separates from alcohol in red needles. Dyes have also been obtained by coupling the diazo-solution with β-naphtholdisulphonic acid, for example, *sodium 4-stilbazole-2′-azo-β-naphtholdisulphonate*, $C_{23}H_{15}O_7N_3S_2Na_2$. Also, *4-stilbazole-2′-azo-resorcinol hydrochloride*, $C_{19}H_{16}O_2N_3Cl$ (yellow); *sodium* salt of *4-stilbazole-2′-azonitro-α-naphthol*, $C_{23}H_{15}O_3N_4Na$ (dark yellow); *sodium 4-stilbazole-2′-azo-β-naphtholsulphonate*, $C_{23}H_{16}O_4N_3SNa$ (red); sodium salt of 4-stilbazole-2′-azo-α-naphthol, $C_{23}H_{17}ON_3Na$ (pale yellow), and the corresponding *sulphonate*, $C_{23}H_{16}O_4N_3SNa$ (yellow.) J. J. S.

Conversion of Acridone into Phenylacridine Derivatives. Fritz Ullmann, Walter Bader, and Hans Labhardt (*Ber.*, 1907, 40, 4795—4799).—Acridones and dimethylaniline condense in the presence of phosphoryl chloride at 100° to form acridines, in which the dimethylaniline radicle is in the para-position to the acridine carbon atom, as shown by colour reactions. The reaction is a general one.

4′-Dimethylamino-9-phenylacridine,



$C_6H_4{<}\genfrac{}{}{0pt}{}{C\text{—}C_6H_4\cdot NMe_2}{N}{>}C_6H_4$

, is obtained in 92% yield, and crystallises from amyl alcohol in yellow aggregates of needles, m. p. 279°; the corresponding *diethyl* compound, $C_{23}H_{22}N_2$, crystallises from petroleum in glistening, yellowish-brown needles, m. p. 197°. *2-Nitroacridone*, $C_{13}H_8O_3N_2$, prepared by heating anhydrous aluminium chloride with the chloride of *m*-nitrodiphenylaminecarboxylic acid in benzene solution, crystallises from nitrobenzene in yellow leaflets, m. p. above 360°, and is converted into *2-nitro-4′-dimethylamino-9-phenylacridine*, $NO_2\cdot C_{13}NH_6\cdot C_6H_4\cdot NMe_2$, a large excess of dimethylaniline being required. It forms red plates from a mixture of benzene and petroleum; m. p. 255°.

2 : 4-*Dinitroacridone*, $C_{13}H_7O_5N_3$, forming orange leaflets, m. p. above 360°, gives a 50% yield of 2 : 4-*dinitro-4′-dimethylamino-9-phenylacridine*, $C_{21}H_{16}O_4N_3$, which crystallises in dark brownish-violet leaflets. W. R.

Condensation of *p*-Phenylenediamine, β-Naphthylamine, and β-Naphthylhydrazine with Aldehydes and Ketones. S. Rothenfusser (*Arch. Pharm.*, 1907, 245, 360—376).—The condensation is effected by warming the substances together in aqueous-alcoholic solution in the case of the first two bases, and in alcoholic solution in the case of β-naphthylhydrazine; each amino-group condenses with a carbonyl group, water being eliminated. The products are crystalline, and yellow to white in colour; a list of them with their m. p.'s is given below. These reactions might be used as a means of detecting the respective aldehydes or ketones in essential oils.

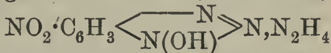
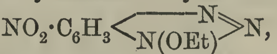
p-Phenylenediamine: with cinnamaldehyde, yellow, 223—224°.

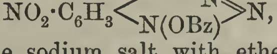
β-Naphthylamine: with cinnamaldehyde, yellow, 125°.

β-Naphthylhydrazine: with citral, white (turns yellow in daylight), 122°; with cinnamaldehyde, yellow, 188°; with anisaldehyde, nearly white, 187°; with piperonal; flesh-coloured, 186°; with vanillin, flesh-coloured, 187°; with carvone, white, 147°. C. F. B.

Action of Hydrazine Hydrate on Nitro-compounds. V. Action of Hydrazine Hydrate on 2 : 4-Dinitrophenylhydrazine. Theodor Curtius and Max Mayer (*J. pr. Chem.*, 1907, [ii], 76, 369—400. Compare Abstr., 1907, i, 969, 970, 1078, 1079).—The action of acid chlorides on 2 : 4-dinitrophenylhydrazine (Curtius and Dedichen, Abstr., 1895, i, 29) in boiling alcoholic solution leads to the formation of *s*-monohydrazides. In this manner have been prepared: *s-benzoyl*-2 : 4-*dinitrophenylhydrazide*, $C_6H_3(NO_2)_2\cdot NH\cdot NHBz$, orange-red leaflets, m. p. 206—207°; *s*-2 : 4 : 6 : 2′ : 4′-pentanitrohydrazobenzene (Ciusa, Abstr., 1907, i, 874), and *s*-acetyl-2 : 4-dinitrophenylhydrazide, m. p. 196—197° (193—194° : Purgotti, Abstr., 1895, i, 27).

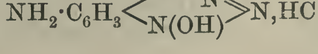
2 : 4-Dinitrophenylhydrazine reacts with dilute alkalis only when heated, but with concentrated alkalis at the ordinary temperature, evolving nitrogen and yielding a brown *product* which is not 2 : 4-dinitrophenol (compare Curtius and Dedichen, *loc. cit.*).

When heated with alcoholic hydrazine hydrate, 2 : 4-dinitrophenylhydrazine evolves small amounts of nitrogen and ammonia, and forms, as the chief product, the *hydrazine* salt,  $NO_2\cdot C_6H_3<\begin{matrix}N\\ N(OH)\end{matrix}>N,N_2H_4$ which crystallises on cooling in small, yellow needles, m. p. 205—206° (decomp.), and dissolves in water to a dark red solution if concentrated, or a yellowish-red if very dilute. 6-Nitro-1-hydroxy-1 : 2 : 3-benzotriazole, $C_6H_4O_3N_4$ (Abstr., 1907, i, 969), formed by the action of hydrochloric or acetic acid on the hydrazine salt, crystallises from water in yellow needles or prisms, or from nitrobenzene in leaflets, detonates at 190—192°, dissolves in aqueous alkalis or alkali carbonates, and is reprecipitated unchanged on dilution of its solution in concentrated sulphuric acid. The *sodium*, $C_6H_3O_3N_4Na$, *potassium*, and *ammonium* salts are described. The solution of the sodium salt gives precipitates with salts of the alkaline earths and heavy metals. The *aniline* salt, $C_6H_4O_3N_4,NH_2Ph$, crystallises in yellow needles, m. p. 159—160°. The *ethyl ether*,  $NO_2\cdot C_6H_3<\begin{matrix}N\\ N(OEt)\end{matrix}>N$, prepared by boiling the sodium salt with alcoholic ethyl iodide, crystallises in yellow needles, m. p. 79—80°. The *methyl ether*, $C_7H_6O_3N_4$, crystallises in white needles, m. p. 129—130°. The *benzyl ether*, $C_{13}H_{10}O_3N_4$, forms prisms, m. p. 115—116°. The *benzoyl* derivative,

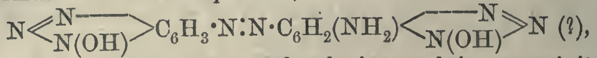


$$NO_2\cdot C_6H_3<\begin{matrix}N\\ N(OBz)\end{matrix}>N,$$

prepared by boiling the sodium salt with ethereal benzoyl chloride, crystallises in white needles, m. p. 160—161°. The *acetyl* derivative is obtained as a white substance, which decomposes on recrystallisation from alcohol. Oxidation of the benzotriazole with permanganate in dilute potassium hydroxide solution leads to the formation of 1-hydroxy-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid, m. p. 152—153° (150° : Zincke and Schwarz, Abstr., 1900, i, 527).

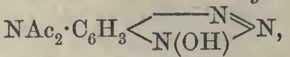
Whilst reduction of the benzotriazole with hydriodic acid at 140—150° leads to the formation of a black, carbonaceous mass from which a definite product cannot be isolated, 6-*amino*-1-*hydroxy*-1 : 2 : 3-*benzotriazole hydrochloride*,  $NH_2\cdot C_6H_3<\begin{matrix}N\\ N(OH)\end{matrix}>N,HCl$, m. p.

220° (decomp.), is prepared by treatment of the nitro-compound or its ethyl ether with tin and hydrochloric acid. This is obtained as a rose-coloured substance, which with silver nitrate forms silver chloride and a gelatinous mass, and when neutralised with sodium hydroxide or ammonia and treated with sodium acetate forms a red solution which slowly deposits a dark, flocculent precipitate. The action of aqueous sodium nitrite on the hydrochloride in neutral solution leads to the formation of a violet *product*,



$$\mathrm{N}\Big\langle\!\!\Big\langle\begin{matrix}\mathrm{N}\text{——}\\ \mathrm{N(OH)}\end{matrix}\Big\rangle\mathrm{C_6H_3{\cdot}N{:}N{\cdot}C_6H_2(NH_2)}\Big\langle\begin{matrix}\text{——}\mathrm{N}\\ \mathrm{N(OH)}\end{matrix}\Big\rangle\!\!\Big\rangle\mathrm{N}\ (?),$$

which dissolves in alkalis to a red solution and is reprecipitated by acids, but in strongly acid solution to the formation of the *diazo*-salt, which with resorcinol gives a brownish-red precipitate dissolving in acids to a Bordeaux-red solution. The *diacetyl* derivative,



$$\mathrm{NAc_2{\cdot}C_6H_3}\Big\langle\begin{matrix}\text{——}\mathrm{N}\\ \mathrm{N(OH)}\end{matrix}\Big\rangle\!\!\Big\rangle\mathrm{N},$$

m. p. about 202° (decomp.), prepared by boiling the hydrochloride with acetic anhydride, decomposes when dissolved in acetic acid, forming 6-*amino*-1-*hydroxy*-1 : 2 : 3-*benzotriazole acetate*, $C_8H_{10}O_3N_4$, which crystallises in prisms, detonating at 235—236°.

When treated with aqueous alkalis or ammonia, or hydrazine hydrate, under varying conditions, 2 : 4 : 6-trinitrophenylhydrazine (Curtius and Dedichen, *loc. cit.*) yields only products which are insoluble in alkalis or indifferent solvents, are not explosive, and hence cannot be dinitro-1-hydroxy-1 : 2 : 3-benzotriazole. G. Y.

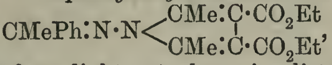
The Amino-groups Attached to the Nitrogen Atom of Heterocyclic Compounds. CARL BÜLOW and EMIL KLEMANN (*Ber.*, 1907, **40**, 4749—4760).—The present research is concerned with the investigation of the *N*-amino-group in ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate (Abstr., 1903, i, 196). The amino-group is replaced by hydrogen when the compound is acted on by nitrous acid, Knorr's ethyl 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate being formed. Whilst the amino-group attached to the *ring carbon* of carboxylic or heterocyclic compounds is transformed in acid solution by means of sodium nitrite into the diazonium group, the amino-group attached to the *ring nitrogen* of heterocyclic compounds is eliminated under similar conditions as nitrous oxide, and is replaced by a hydrogen atom. The reactivity of the *N*-amino-group of the pyrrole derivative under consideration is much less than that of a primary *C*-amine or of a secondary hydrazine. Whilst, for example, secondary hydrazines, as a class, easily interact with aromatic aldehydes and ketones, ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate couples with aldehydes only after boiling for several hours in ethyl-alcoholic solution, whilst it reacts with ketones even with greater difficulty.

Ethyl benzylideneamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, $C_{19}H_{22}O_4N_2$, obtained by boiling ethyl amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate for eight hours with a mixture of benzaldehyde and ethyl alcohol, separates from dilute alcohol in prisms, m. p. 49°; when boiled with dilute acetic acid, benzaldehyde is eliminated.

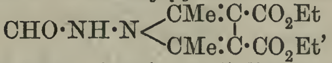
Ethyl p-*hydroxybenzylideneamino*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarb*-

oxylate, $C_{19}H_{22}O_5N$, obtained in a similar manner from *p*-hydroxybenzaldehyde, has m. p. 154°.

Ethyl 1-propylideneamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, $CMe_2{:}N{\cdot}CNMe_2(CO_2Et)_2$, obtained by heating ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate with acetone for ten hours at 100° in a sealed tube, is an oil, b. p. 247—253°/60 mm.

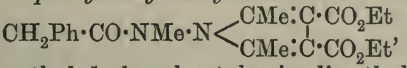
Ethyl 1-α-phenylethylideneamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate,  $CMePh{:}N{\cdot}N{<}\begin{array}{l}CMe{:}C{\cdot}CO_2Et\\ CMe{:}C{\cdot}CO_2Et\end{array}$, obtained from acetophenone, separates from light petroleum in glistening plates, m. p. 111—112°.

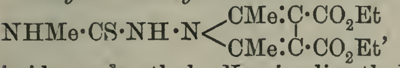
Ethyl 1-formylamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate,

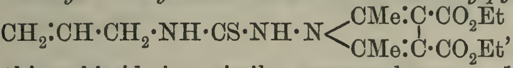


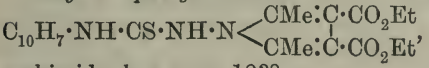
$$CHO{\cdot}NH{\cdot}N{<}\begin{array}{l}CMe{:}C{\cdot}CO_2Et\\ CMe{:}C{\cdot}CO_2Et\end{array},$$

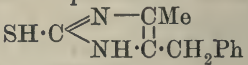
obtained by heating ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate with anhydrous formic acid, crystallises in needles, m. p. 139°. The same compound is obtained when formylhydrazide acts on ethyl diacetylsuccinate. When partially saponified at the ordinary temperature, the operation may be conducted so that only one of the oxyethyl-groups is eliminated with the formation of *monoethyl 1-formylamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate*, $C_{11}H_{14}O_5N_2$, which decomposes at 150°.

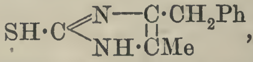
Ethyl 1-phenylacetylmethylamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate,  $CH_2Ph{\cdot}CO{\cdot}NMe{\cdot}N{<}\begin{array}{l}CMe{:}C{\cdot}CO_2Et\\ CMe{:}C{\cdot}CO_2Et\end{array}$, obtained by the methylation of ethyl 1-phenylacetylaminodimethylpyrroledicarboxylate by means of methyl sulphate, is insoluble in dilute alkali, and separates from light petroleum in prisms or plates, m. p. 82°.

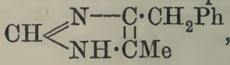
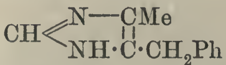
Ethyl 1-methylthiocarbamido-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate,  $NHMe{\cdot}CS{\cdot}NH{\cdot}N{<}\begin{array}{l}CMe{:}C{\cdot}CO_2Et\\ CMe{:}C{\cdot}CO_2Et\end{array}$, obtained from methylthiocarbimide and ethyl *N*-aminodimethylpyrroledicarboxylate, has m. p. 193—194°.

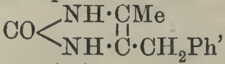
Ethyl 1-allylthiocarbamido-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate,  $CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}N{<}\begin{array}{l}CMe{:}C{\cdot}CO_2Et\\ CMe{:}C{\cdot}CO_2Et\end{array}$, obtained from allylthiocarbimide in a similar manner, has m. p. 192°.

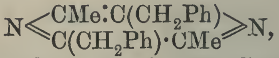
Ethyl α-naphthylthiocarbamido-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate,  $C_{10}H_7{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}N{<}\begin{array}{l}CMe{:}C{\cdot}CO_2Et\\ CMe{:}C{\cdot}CO_2Et\end{array}$, obtained from naphthylthiocarbimide, has m. p. 183°. A. McK.

α-Amino-α-benzylacetone. ADOLF SONN (*Ber.*, 1907, 40, 4666—4670).—*α-Amino-α-benzylacetone* is obtained in the form of its *hydrochloride*, $COMe{\cdot}CH(CH_2Ph){\cdot}NH_2,HCl$, white leaflets, m. p. 126—127°, after sintering at 124°, by the reduction of α-*iso*nitroso-α-benzylacetone with tin and hydrochloric acid ; the *platinichloride*, $(C_{10}H_{13}ON)_2,H_2PtCl_6$, small, orange, spear-shaped crystals, m. p. 185—186° (decomp.) ; the crystalline *aurichloride*, $C_{10}H_{13}ON,HAuCl_4$, m. p. 136°, and *picrate*, $C_{10}H_{13}ON,C_6H_2(NO_2)_3OH$, small, yellow octahedra, m. p. 147°, were prepared. The hydrochloride when warmed with an aqueous solution of potassium thiocyanate yields *benzylmethylglyoxaline mercaptan*,  $\mathrm{SH{\cdot}C}\left<\begin{array}{l}\mathrm{N{-}CMe}\\ \mathrm{NH{\cdot}C{\cdot}CH_2Ph}\end{array}\right.$ or

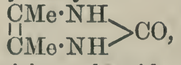
 $\mathrm{SH{\cdot}C}\left<\begin{array}{l}\mathrm{N{-}C{\cdot}CH_2Ph}\\ \mathrm{NH{\cdot}CMe}\end{array}\right.$,

crystallising in white leaflets, decomposing at 260° (approx.); it has a bitter taste, and evolves sulphur dioxide with concentrated sulphuric acid. Oxidation with hot 10% nitric acid converts it into a compound which is either *4-benzyl-5-methylglyoxaline*,  $\mathrm{CH}\left<\begin{array}{l}\mathrm{N{-}C{\cdot}CH_2Ph}\\ \mathrm{NH{\cdot}CMe}\end{array}\right.$, or *5-benzyl-4-methylglyoxaline*,  $\mathrm{CH}\left<\begin{array}{l}\mathrm{N{-}CMe}\\ \mathrm{NH{\cdot}C{\cdot}CH_2Ph}\end{array}\right.$ (compare Gabriel and Pinkus, Abstr., 1893, i, 734). It crystallises in small tufts of needles, m. p. 132°; the *aurichloride*, $C_{11}H_{12}N,HAuCl_4$, forms yellow needles, m. p. 157°; the *picrate*, $C_{11}H_{12}N,C_6H_2(NO_2)_3OH$, crystallises in yellow plates, m. p. 147°.

α-Amino-α-benzylacetone hydrochloride (1 mol.) interacts with potassium cyanate (1 mol.) in aqueous solution with the formation of 4 : 5-*benzylmethylglyoxaline*,  $\mathrm{CO}\left<\begin{array}{l}\mathrm{NH{\cdot}CMe}\\ \mathrm{NH{\cdot}C{\cdot}CH_2Ph}\end{array}\right.$, white leaflets, turning brown at 220° (approx.), m. p. 270°.

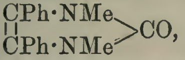
3 : 6-*Dibenzyl-2 : 5-dimethylpyrazine*,  $\mathrm{N}\left<\begin{array}{l}\mathrm{CMe{:}C(CH_2Ph)}\\ \mathrm{C(CH_2Ph){\cdot}CMe}\end{array}\right>\mathrm{N}$, is formed by the oxidation of α-amino-α-benzylacetone; it crystallises in large, slightly yellow prisms, m. p. 97—98°; the *platinichloride*, $(C_{20}H_{20}N_2)_2,H_2PtCl_6$, forms reddish-yellow crystals, m. p. 197—198°; the *aurichloride*, $C_{20}H_{20}N_2,HAuCl_4$, crystallises in rhombic prisms, m. p. 164—165° (decomp.); the *picrate*, $C_{20}H_{20}N_2,C_6H_3O_7N_3$, forms yellow crystals, m. p. 125—126°. 3 : 6-Dibenzyl-2 : 5-dimethylpyrazine is converted on oxidation with chromic acid into 3 : 6-*dibenzoyl*-2 : 5-*dimethylpyrazine*, $C_4N_2Me_2Bz_2$, pale yellow leaflets, m. p. 159—160°; the *dioxime*, $C_4N_2Me_2(CPh{:}N{\cdot}OH)_2$, forms white needles, decomposing at 233°. W. H. G.

Glyoxalones; Iminazolones. HEINRICH BILTZ [with P. HORRMANN] (*Ber.*, 1907, **40**, 4799—4806. Compare Abstr., 1905, i, 674).—Further disubstituted glyoxalones have been prepared and characterised by means of their acetates. With the exception of Rupe's phenylglyoxalone (compare Abstr., 1895, i, 218), it is found that in all the cases in the literature, or in those examined in the present communication, wherever two imino-groups are separated by a carbonyl group, both are acetylated. If, however, an imino-group is situated between two carbonyl groups, then the iminic hydrogen is apparently not replaceable by acetyl.

4 : 5-*Dimethylglyoxalone*  $\begin{array}{l}\mathrm{CMe{\cdot}NH}\\ \mathrm{CMe{\cdot}NH}\end{array}\!\!>\mathrm{CO}$, obtained readily by heating acetylmethylcarbinol with carbamide in anhydrous acetic acid solution, is crystalline, has no m. p., but turns brown at 290° and at

354—355° decomposes. This may or may not be identical with Künne's dimethylglyoxalone (Abstr., 1895, i, 685). The *diacetate*, $C_9H_{12}O_3N_2$, crystallises from alcohol in needles, m. p. 117—118°.

Attempts to condense acetylmethylcarbinol with methylcarbamide and *s*-dimethylcarbamide were unsuccessful.

It is more convenient to use anhydrous glacial acetic acid in the preparation of 4 : 5-diphenyl-3-methylglyoxalone (compare Anschütz and Müller, Abstr., 1895, i, 305). The *acetate*, $C_{18}H_{16}O_2N_2$, forms needles, m. p. 134°. 4 : 5-*Diphenyl*-1 : 3-*dimethylglyoxalone*,  $\left.\begin{array}{l}\text{CPh}\cdot\text{NMe}\\ \parallel\\ \text{CPh}\cdot\text{NMe}\end{array}\right>\text{CO}$, obtained by heating *s*-dimethylcarbamide and benzoin in anhydrous acetic acid solution at 140—150° for four hours, crystallises in prisms, m. p. 185°. There is, therefore, a decrease in the m. p. with the introduction of methyl groups.

Benzoin and *as*-dimethylcarbamide on heating in acetic acid give diphenylglyoxalone, the two methyl groups being eliminated.

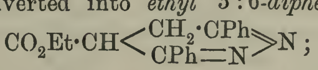
Anschütz and Schwickerath (Abstr., 1895, i, 304) observed that diphenylglyoxalone gives a cherry-red colour with sulphuric acid; this is not characteristic of the substance, as a preparation precipitated from its sulphuric acid solution by water and recrystallisation no longer gave the coloration.

2 : 4 : 5-Triphenylglyoxaline does not form an acetate. W. R.

Pyridazine Synthesis. V. Diphenylpyridazine Derivatives. Carl Paal and Gustav Kühn (*Ber.*, 1907, **40**, 4598—4604. Compare Abstr., 1903, i, 289, 290, 722; 1905, i, 91).—In continuation of work on the behaviour of hydrazine hydrate towards γ-diketones and γ-diketonic esters, the authors have studied the formation of some diphenylpyridazine derivatives.

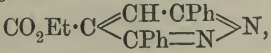
Ethyl phenacylbenzoylacetate monohydrazone,

$$NH_2\cdot N:CPh\cdot CH_2\cdot CH(COPh)\cdot CO_2Et,$$

obtained by the addition of hydrazine hydrate to an alcoholic solution of ethyl phenacylbenzoylacetate, separates in yellowish-white needles, m. p. 125—126°. When heated above its melting point, it loses water and is converted into *ethyl* 3 : 6-*diphenyl*-4 : 5-*dihydropyridazine*-4-*carboxylate*,  $CO_2Et\cdot CH\left<\begin{array}{l}CH_2\cdot CPh\\ CPh{=}N\end{array}\right>N$; the latter compound may also be formed directly from ethyl phenacylbenzoylacetate and hydrazine hydrate in glacial acetic acid solution; it crystallises from dilute alcohol in greenish-yellow needles, m. p. 116—117°, and is characterised by conversion into 3 : 6-diphenylpyridazine.

3 : 6-*Diphenyldihydropyridazine*-4-*carboxylic acid*, $C_{17}H_{14}O_2N_2$, obtained by the action of alcoholic potassium hydroxide either on the preceding ester or on the hydrazone already described, separates from aqueous alcohol in colourless needles, m. p. 205—206°. Attempts to prepare 3 : 6-diphenyldihydropyridazine by heating this acid were not successful.

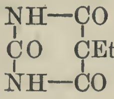
Ethyl 3 : 6-*diphenylpyridazine*-4-*carboxylate*,



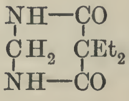
$$CO_2Et\cdot C\left<\begin{array}{l}CH\cdot CPh\\ CPh{=}N\end{array}\right>N,$$

obtained by oxidising the dihydro-ester with nitrous acid, crystallises in needles, m. p. 98—99°. When saponified, it forms 3 : 6-*diphenylpyridazine-4-carboxylic acid*, $C_{17}H_{12}O_2N_2$, which separates from aqueous alcohol in colourless needles, m. p. 220—221° (decomp.); in contradistinction to the dihydro-acid, this acid readily loses carbon dioxide and forms 3 : 6-diphenylpyridazine. A. McK.

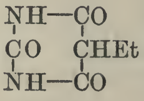
Electrolytic Reduction of Ethylbarbituric Acid. JULIUS TAFEL and HERBERT BRYAN THOMPSON (*Ber.*, 1907, 40, 4489—4497). —Tafel and Weinschenk have shown (Abstr., 1901, i, 72) that electrolytic reduction of barbituric acid leads to the formation of hydrouracil. It is now found that 5 : 5-diethylbarbituric acid (veronal) (I) on electrolytic reduction yields 4 : 6-diketo-5 : 5-diethylhexahydropyrimidine (2-deoxyveronal) (II), together with a small amount of a yellow resin, whereas, under similar conditions, 5-ethylbarbituric acid (III) yields 5-ethylhydrouracil (IV) and 5-ethyltrimethylenecarbamide (V).


$\begin{array}{ll} NH & \!\!—CO \\ CO & CEt_2 \\ NH & \!\!—CO \end{array}$

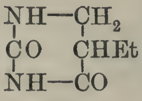
(I.)


$\begin{array}{ll} NH & \!\!—CO \\ CH_2 & CEt_2 \\ NH & \!\!—CO \end{array}$

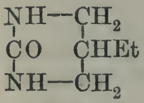
(II.)


$\begin{array}{ll} NH & \!\!—CO \\ CO & CHEt \\ NH & \!\!—CO \end{array}$

(III.)


$\begin{array}{ll} NH & \!\!—CH_2 \\ CO & CHEt \\ NH & \!\!—CO \end{array}$

(IV.)


$\begin{array}{ll} NH & \!\!—CH_2 \\ CO & CHEt \\ NH & \!\!—CH_2 \end{array}$

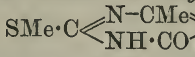
(V.)

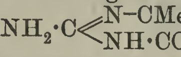
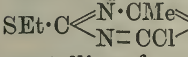
On reduction in 75% sulphuric acid solution with a current density of 30 amperes and lead electrodes at 48—53° for seven hours, veronal yields 90% of its weight of 4 : 6-*diketo*-5 : 5-*diethylhexahydropyrimidine*, which crystallises from ethyl acetate in leaflets, m. p. 292°, sublimes when quickly heated, is readily soluble in cold dilute alkalis, and on hydrolysis with baryta at 140° forms a mixture of diethylmalonic and diethylmalonamic acids. When heated with bromine in glacial acetic acid at 100°, diethylhexahydropyrimidine yields ammonium bromide and formic and diethylmalonamic acids. Formic and diethylmalonic acids are formed by hydrolysis of the yellow resin obtained on reduction of veronal.

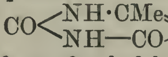
Diethylmalonamic acid, $NH_2 \cdot CO \cdot CEt_2 \cdot CO_2H$, separates from water in crystals, m. p. 144°, and yields diethylmalonic acid when treated with sodium nitrite in concentrated sulphuric acid solution at 100°, or on prolonged boiling with concentrated aqueous baryta.

5-*Ethylhydrouracil*, prepared by reduction of 5-ethylbarbituric acid with a current density of 15 amperes at 7—15° for four hours, crystallises from water in colourless leaflets, m. p. 274°, sublimes when quickly heated, is neutral in aqueous solution, and is only sparingly soluble in dilute sodium hydroxide. On successive treatment with bromine in 15% glacial acetic acid solution at 100° and sodium hydroxide, 5-ethylhydrouracil yields 5-ethyluracil, which separates on acidification of the alkaline solution and crystallises from methyl alcohol in needles, m. p. 303°.

5-Ethyltrimethylenecarbamide, prepared by reduction of 5-ethylbarbituric acid with a current density of 12 amperes at 38—45°, is isolated in the form of its *picrate*, $C_{12}H_{15}O_8N_5$, m. p. 131—133°. The free carbamide crystallises in prisms, m. p. 170°. G. Y.

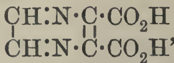
Pyrimidines. XXVIII. Synthesis of 4-Methyluracil-5-acetic Acid. TREAT B. JOHNSON and FREDERICK W. HEYL (*Amer. Chem. J.*, 1907, 38, 659—670).—It has been shown in a previous paper (Abstr., 1907, i, 1083) that ethyl formylsuccinate condenses readily with ψ-ethylthiocarbamide to form ethyl 6-oxy-2-ethylthiolpyrimidine-5-acetate, which can be converted easily into thymine-5-carboxylic acid. It is now shown that 4-methyluracil-5-acetic acid can be prepared in a quite analogous manner from ψ-ethylthiocarbamide and ethyl acetylsuccinate. 6-*Oxy*-2-*methylthiol*-4-*methylpyrimidine*-5-*acetic acid*,  $\mathrm{SMe{\cdot}C}{<}\begin{array}{l}\mathrm{N{-}CMe}\\ \mathrm{NH{\cdot}CO}\end{array}{>}\mathrm{C{\cdot}CH_2{\cdot}CO_2H}$, is formed when ψ-methylthiocarbamide hydriodide is treated with ethyl acetylsuccinate in presence of potassium hydroxide solution. It sinters at 260°, decomposes at 270—272°, and crystallises from hot water or alcohol in flat prisms.

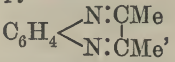
6-*Oxy*-2-*ethylthiol*-4-*methylpyrimidine*-5-*acetic acid*, m. p. 255° (decomp.), similarly prepared, crystallises in long prisms from boiling benzonitrile or nitrobenzene. The *potassium* salt is crystalline. The *ethyl* ester, m. p. 163—165°, formed in the usual manner with some *ethyl* 4-*methyluracil*-5-*acetate* (see below) as a by-product, crystallises from alcohol in hair-like needles. When the acid is heated with ammonia in alcohol at 170—180° during four hours, 2-*amino*-6-*oxy*-4-*methylpyrimidine*-5-*acetic acid*,  $\mathrm{NH_2{\cdot}C}{<}\begin{array}{l}\mathrm{N{-}CMe}\\ \mathrm{NH{\cdot}CO}\end{array}{>}\mathrm{C{\cdot}CH_2{\cdot}CO_2H}$, m. p. 322° (decomp.), is produced. It crystallises from water in needles. On digesting the acid at 100° with phosphoryl chloride and pouring the product into cold ammonia in alcohol, 6-*chloro*-2-*ethylthiol*-4-*methylpyrimidine*-5-*acetamide*, m. p. 167° (decomp.), crystallising from water in sheaves, is formed, but if the reaction mixture be poured on ice there is produced 6-*chloro*-2-*ethylthiol*-4-*methylpyrimidine*-5-*acetic acid*,  $\mathrm{SEt{\cdot}C}{<}\begin{array}{l}\mathrm{N{\cdot}CMe}\\ \mathrm{N{=}CCl}\end{array}{>}\mathrm{C{\cdot}CH_2{\cdot}CO_2H}$, m. p. 118—119° (decomp.), which crystallises from hot water in needles. Alcoholic ammonia only reacts with the latter substance when heated with it at 125—135°, and then forms 6-*amino*-2-*ethylthiol*-4-*methylpyrimidine*-5-*acetic acid*, m. p. 221°, crystallising from alcohol in beautiful needles. When the reaction is conducted at 167—180°, the action goes further, and 2 : 6-*diamino*-4-*methylpyrimidine*-5-*acetic acid*, m. p. 279—280° (decomp.), crystallising in small prisms from hot water, is formed.

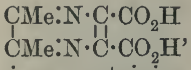
4-*Methyluracil*-5-*acetic acid*,  $\mathrm{CO}{<}\begin{array}{l}\mathrm{NH{\cdot}CMe}\\ \mathrm{NH{-}CO}\end{array}{>}\mathrm{C{\cdot}CH_2{\cdot}CO_2H}$, m. p. 340° (decomp.), is formed when 6-oxy-2-ethylthiol-4-methylpyrimidine-5-acetic acid is boiled with hydrochloric acid. It crystallises from hot water in long prisms, sinters at 329°, decomposes at 340°, is soluble in water to the extent of 0·0894% to 0·0901%, and is unaffected by heating with dilute sulphuric acid (20%) during two hours at 153—173°. The *lead*, *potassium*, and *barium* salts are crystalline, and the *silver* salt amorphous. The *ethyl* ester, m. p. 221—222°, crystallises in needles from alcohol; the *methyl* ester melts at 280—282°.

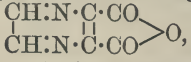
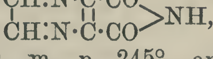
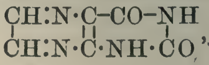
T. A. H.

Formation of Pyrazine Compounds from Quinoxaline Derivatives. SIEGFRIED GABRIEL and ADOLF SONN (*Ber.*, 1907, 40, 4850—4860).—Quinoxaline and its 2 : 3-dimethyl derivatives are oxidised to pyrazine 2 : 3-dicarboxylic acid and 5 : 6-dimethylpyrazine-2 : 3-dicarboxylic acid when heated with a 2% permanganate solution in the presence of potassium hydroxide.

Pyrazine-2 : 3-*dicarboxylic acid*,  $\begin{array}{l}CH{:}N{\cdot}C{\cdot}CO_2H\\ CH{:}N{\cdot}C{\cdot}CO_2H\end{array}$, crystallises from water in colourless, glistening prisms containing $2H_2O$; when heated, it gives up water and melts and decomposes at 186°, whereas the anhydrous acid has m. p. 193° (decomp.). The *barium*, *lead*, *cupric*, and *silver* salts are sparingly soluble. When heated with glacial acetic acid at 180°, the acid yields pyrazine.

2 : 3-*Dimethylquinoxaline*,  $C_6H_4{<}\begin{array}{l}N{:}CMe\\ N{:}CMe\end{array}$, is readily prepared by the condensation of *o*-phenylenediamine acetate with diacetylmonoxime in warm aqueous solution. It crystallises from water in slender, glistening needles containing water of crystallisation, which it loses on exposure to the air. When rapidly heated, the crystals melt at 85°, resolidify, and melt a second time at 104—106°. The *platinichloride*, $(C_{10}H_{10}N_2)_2,H_2PtCl_6$, forms orange-red prisms; the *aurichloride*, a yellow precipitate, which sinters at 90—95° and decomposes at 130°; the *picrate* has m. p. 189°.

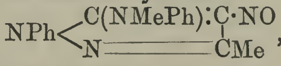
2 : 3-*Dimethylpyrazine*-5 : 6-*dicarboxylic acid*,  $\begin{array}{l}CMe{:}N{\cdot}C{\cdot}CO_2H\\ CMe{:}N{\cdot}C{\cdot}CO_2H\end{array}$, crystallises from hot water in glistening, rhombic prisms containing $2H_2O$. When anhydrous, it melts and decomposes at 200°. The *barium* salt forms sparingly soluble needles. The *cupric*, *lead*, and *silver* salts are also sparingly soluble. When heated with acetic acid at 180°, the acid yields 2 : 3-dimethylpyrazine (Jorre, *Inaug. Diss.*, *Kiel*, 1897), the picrate of which has m. p. 150°. When the dicarboxylic acids are distilled, the chief products are the monobasic acids. Pyrazinecarboxylic acid has m. p. 222° (Stöhr gives 229°). 2 : 3-*Dimethylpyrazine*-5-*carboxylic acid* crystallises in slender needles, m. p. 182°, and produces an orange coloration with ferric chloride.

The *anhydride*,  $\begin{array}{l}CH{:}N{\cdot}C{\cdot}CO\\ CH{:}N{\cdot}C{\cdot}CO\end{array}{>}O$, prepared by the action of thionyl chloride or acetic anhydride on the dicarboxylic acid, crystallises in slender needles and decomposes at about 170°. The *methyl* ester, $C_4H_2N_2(CO_2Me)_2$, forms colourless needles, which sinter at 47° and melt at 50°. The *diamide*, $C_4H_2N_2{\cdot}(CO{\cdot}NH_2)_2$, obtained by the action of a methyl-alcoholic solution of ammonia on the ester, crystallises from hot water in minute octahedra, m. p. 240° (decomp.). The *imide*,  $\begin{array}{l}CH{:}N{\cdot}C{\cdot}CO\\ CH{:}N{\cdot}C{\cdot}CO\end{array}{>}NH$, crystallises from hot alcohol in flat prisms, m. p. 245°, and is soluble in dilute alkalis or ammonia. When the diamide is warmed with bromine and potassium hydroxide solution, the *compound*,  $\begin{array}{l}CH{:}N{\cdot}C{-}CO{-}NH\\ CH{:}N{\cdot}C{\cdot}NH{\cdot}CO\end{array}$, is obtained. It crystallises from hot water in long prisms, which are not molten at 300°, and possesses acidic properties. When the diamide is warmed with 1 gram-molecule of hypobromite, 2-*amino-pyrazine-3-carboxylic* acid, $NH_2{\cdot}C_4H_2N_2{\cdot}CO_2H$, is obtained. This crystallises from hot water in felted needles, m. p. 209—210° (decomp.). When heated slightly above its melting point, the amino-acid yields 2-*aminopyrazine*, $C_4H_3N_2{\cdot}NH_2$, in the form of yellow crystals, which sinter at 110°, and melt to a clear liquid at 117°. The *picrate* is sparingly soluble and has no definite m. p. The *hydrochloride* forms pointed needles, sparingly soluble in concentrated hydrochloric acid; the *hydriodide*, dark brown prisms; the *aurichloride*, sparingly soluble, short prisms, and the *mercurichloride*, colourless needles. J. J. S.

Nitroso-compounds of ψ-Pyrines, and 2-Alkylanilopyrines.

August Michaelis and Georg Mielecke (*Ber.*, 1907, 40, 4482—4488).—Whilst in the pyrine series nitroso-derivatives have been obtained from antipyrines but not from thio-, seleno-, or anilo-pyrines, nitroso-derivatives of ψ-thiopyrines have been described by Michaelis and Dorn (Abstr., 1907, i, 246), and of ψ-selenopyrines by Michaelis and von der Hagen (*ibid.*, 249). In continuation of this work, it is now found that ψ-antipyrines and ψ-anilopyrines yield similar, intensely green nitroso-derivatives. Thus 5-ethoxy-1-phenyl-3-methylpyrazole (ψ-ethylantipyrine), when treated with sodium nitrite in glacial acetic acid, yields an intensely green solution, depositing on addition of water a green *oil* which rapidly darkens. It has not yet been found possible to obtain such nitroso-ψ-antipyrines in the crystalline state. Nitroso-ψ-anilopyrines, on the other hand, readily crystallise, and with phenol in sulphuric acid solution give a red coloration, becoming green on addition of water and excess of sodium hydroxide.

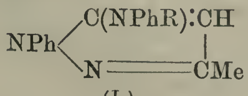
4-*Nitroso-ψ-anilopyrine*,



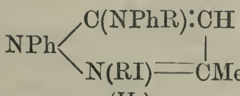
$$\mathrm{NPh}\Big<\begin{matrix}\mathrm{C(NMePh){:}C{\cdot}NO}\\ \qquad\qquad\quad |\\ \mathrm{N{=\!=\!=\!=\!=}CMe}\end{matrix}$$

, prepared by addition of concentrated aqueous sodium nitrite to a glacial acetic acid solution of ψ-anilopyrine, crystallises in dark green leaflets, m. p. 89°. The *hydrochloride*, $C_{17}H_{16}N_3{\cdot}NO,HCl$, m. p. 156° (decomp.), loses HCl becoming green, slowly on exposure to air or rapidly on treatment with water.

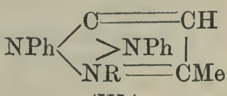
The homologues of ψ-anilopyrine (I) are prepared by distillation of the corresponding alkyliodides (II) of the 2-alkylanilopyrines (III), which are obtained by successive action of phosphoryl chloride and aniline on the 2-alkylantipyrines (Abstr., 1904, i, 112), or of the alkyliodide and sodium hydroxide on 5-anilino-1-phenyl-3-methyl-pyrazole.



(I.)



(II.)



(III.)

2-*Ethylanilopyrine*, $C_{18}H_{19}N_3$, forms strongly refracting, monoclinic crystals, m. p. 69·5°, b. p. 230°/22 mm. (slight decomp.), and has an alkaline reaction to alcoholic litmus. The *hydrochloride* crystallises in hygroscopic needles; the *platinichloride*, $(C_{18}H_{19}N_3)_2,H_2PtCl_6$, yellow leaflets, m. p. 199°; the *hydriodide*, white needles, m. p. 182°; the *picrate*, yellow leaflets, m. p. 131°; the *chromate*, golden leaflets, m. p. 178°; the *methiodide*, white needles, m. p. 159°; the *ethiodide*, $C_{18}H_{19}N_3,EtI$, large, transparent crystals, m. p. 146°; the *propiodide*, white leaflets, m. p. 107°; the *benzoyl iodide*, m. p. 187°; the *acetyl iodide*, m. p. 180·5°.

ψ-Ethylanilopyrine, $C_{18}H_{19}N_3$, is obtained as a yellow oil, b. p. 235°/20 mm., is neutral, dissolves in dilute hydrochloric acid, but is reprecipitated on addition of water, and when heated with ethyl iodide yields 2-ethylanilopyrine ethiodide. The *platinichloride*,

$$(C_{18}H_{19}N_3)_2,H_2PtCl_6,$$

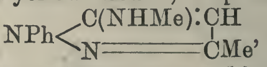
forms yellow leaflets, m. p. 189°. The 4-*nitroso*-derivative is obtained in dark green crystals, m. p. 98°, and forms a *hydrochloride* crystallising in yellow needles, m. p. 140° (decomp.).

2-n-*Propylanilopyrine*, $C_{19}H_{21}N_3$, crystallises in yellow needles, m. p. 50°, and is strongly alkaline. The *platinichloride*, m. p. 197°, *hydriodide*, m. p. 173·5°, *methiodide*, m. p. 179°, *ethiodide*, m. p. 118°, and *propiodide*, m. p. 154—155°, are described.

ψ-n-*Propylanilopyrine* forms monoclinic crystals, m. p. 74°; the *platinichloride*, m. p. 156°. The 4-*nitroso*-derivative, $C_{19}H_{20}N_3\cdot NO$, is obtained in green crystals, m. p. 73°, and forms a yellow *hydrochloride*, m. p. 129°.

2-*Benzylanilopyrine*, $C_{23}H_{21}N_3$, obtained in small yields by heating 5-anilino-1-phenyl-3-methylpyrazole with benzyl chloride at 150° and treatment of the product with sodium hydroxide, crystallises in yellow needles, m. p. 84°, and has a strong alkaline reaction. The *hydrochloride*, $C_{23}H_{21}N_3,HCl$, m. p. 99°, *platinichloride*, m. p. 206°, *hydriodide*, m. p. 169°, *chromate*, m. p. 172°, *methiodide*, m. p. 137°, *ethiodide*, m. p. 149°, *propiodide*, m. p. 159°, and *benzoylchloride* $(+2H_2O)$, m. p. 75°, are described.

ψ-Benzylanilopyrine, $C_{23}H_{21}N_3$, crystallises in yellow leaflets, m. p. 83°, b. p. 260°/18 mm., and is neutral. The *platinichloride* crystallises in golden needles, m. p. 171°. The 4-*nitroso*-derivative, $C_{23}H_{20}N_3\cdot NO$, crystallises in green needles, m. p. 70°, and forms a *hydrochloride*, $C_{23}H_{20}N_3\cdot NO,HCl$, crystallising in yellow needles, m. p. 134°.

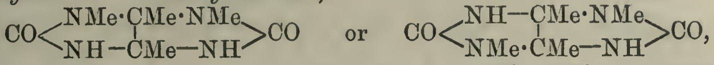
[With LUTZE.]—*ψ-Iminopyrine*,  $NPh<\begin{array}{l}C(NHMe):CH\\ N=\!=\!=\!=\!=CMe\end{array}$, prepared by distillation of iminopyrine methiodide (Stolz, Abstr., 1904, i, 113), is obtained as a colourless oil, and forms a 4-*nitroso*-derivative which separates from ether in green crystals, m. p. 139°. G. Y.

Diureines. HEINRICH BILTZ [with P. HORRMANN] (*Ber.*, 1907, 40, 4806—4816).—A study of the behaviour of diureines towards acetic anhydride, as diureines may be considered to be diglyoxalones (compare this vol., i, 56). Acetylenecarbamide (Schiff, Abstr., 1878, 287; Pinner, Abstr., 1884, 1298) gives a *tetra-acetate*,

$$C_{12}H_{14}O_6N_4,$$

which crystallises from alcohol in needles, m. p. 236—238°. Dimethylacetylenediureine (Franchimont and Klobbe, Abstr., 1888, 1180; 1889, 126), however, does not yield an acetate.

The condensation of methylcarbamide and diacetyl gives *dimethylacetylene*-N : N′-*dimethyldiureine*,



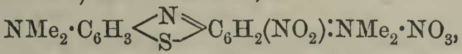
$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NMe\cdot CMe\cdot NMe}\\ \mathrm{NH-CMe-NH}\end{matrix}\right\rangle\mathrm{CO} \quad \text{or} \quad \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH-CMe\cdot NMe}\\ \mathrm{NMe\cdot CMe-NH}\end{matrix}\right\rangle\mathrm{CO},$$

crystallising in prisms or needles, decomp. 305—306°. It gives a *monoacetate*, $C_{10}H_{16}O_3N_4$, needles, m.p. 174—175°. *s*-Dimethylcarbamide and diacetyl gives rise to a product, decomp. 165°, which has not yet been identified.

Diphenylacetylenediureine (Angeli, Abstr., 1890, 1290; Anschütz and Geldermann, 1891, 725) gives a *diacetate*, $C_{20}H_{18}O_4N_4$, crystallising from acetic acid in flat prisms, m. p. 299—301° (Angeli, *loc. cit.*, gives 266°). W. R.

Thiazines. I. Derivatives of Methylene-blue. Robert Gnehm [and Emil Walder] (*J. pr. Chem.*, 1907, [ii], 76, 401—427. Compare Abstr., 1904, i, 687, 935; 1906, i, 211, 389, 390; Kehrmann, Abstr., 1902, i, 566).—The preparation of disulphides of the thiazine series has been undertaken with the object of throwing light on the relation of the thiazines to certain blue sulphur dyes. The method of preparation adopted consists of the nitration of thiazines, reduction of the nitro-compounds to amines, and conversion of these into the corresponding halogen substitution products and mercaptothiazines, which yield disulphides on oxidation.

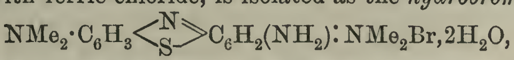
Details are now given of the preparation of methylene-green (nitromethylene-blue) and its nitrate,



$$\mathrm{NMe_2\cdot C_6H_3}\left\langle\begin{matrix}\mathrm{N}\\ \mathrm{S}\end{matrix}\right\rangle\mathrm{C_6H_2(NO_2)\colon NMe_2\cdot NO_3},$$

and hydrobromide from methylene-blue (Gnehm and Walder, Abstr., 1906, i, 390). The dye does not give the nitroso-reactions and must be a nitro-compound, as the hydrobromide requires 4 mols. of hydrogen for complete reduction by means of tin and hydrochloric acid.

Aminomethylene-blue, prepared by reduction of the nitro-compound by means of zinc dust and acetic acid and oxidation of the resulting *leuco-base* with ferric chloride, is isolated as the *hydrobromide*,



$$\mathrm{NMe_2\cdot C_6H_3}\left\langle\begin{matrix}\mathrm{N}\\ \mathrm{S}\end{matrix}\right\rangle\mathrm{C_6H_2(NH_2)\colon NMe_2Br,2H_2O},$$

which forms olive-green crystals, or as the *hydriodide*,

$$C_{16}H_{19}N_4SI,1\tfrac{1}{2}H_2O,$$

which crystallises in microscopic, olive-green needles, violet by transmitted light. The free base dissolves in water, alcohols, or glacial acetic acid, forming a blue, or if concentrated a violet-blue, solution with a slight fluorescence, and dyes silk and cotton mordanted with tannin with a stronger and more violet shade than methylene-blue.

On diazotisation, the amino-dye yields an unstable, greyish-violet solution, which slowly evolves nitrogen, becoming blue. When coupled with *R*-salt in ammoniacal solution, the diazotised dye yields a mixture of a violet *azo-dye*, which dyes silk and wool in a sulphuric acid bath, and a blue dye (hydroxymethylene-blue?), which dyes mordanted cotton and silk in an ammoniacal, or silk in an acetic acid, bath. With β-naphthol in ammoniacal solution, the diazotised dye forms a violet-blue, or with dimethylaniline in an acetic acid solution a greenish-blue, *azo-dye*.

Iodomethylene-blue iodide, $NMe_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{N}{S\text{-}}>C_6H_2I\colon NMe_2I,\frac{1}{2}H_2O$, prepared by the action of potassium iodide on diazotised aminomethylene-blue, crystallises in microscopic, brownish-violet needles; the *chromate* and *mercurichloride* are precipitated quantitatively even from the most dilute solutions.

Attempts to prepare bromomethylene-blue from the diazotised amino-dye led to the formation of a product containing only traces of halogen. The action of potassium xanthate, alcoholic potassium sulphide, and cuprous sodium thiosulphate on diazotised aminomethylene-blue leads to the formation of *dyes* which differ from the typical sulphur dyes in that they are readily reduced by sodium sulphide in the cold.

Hydroxymethylene-blue, formed when diazotised aminomethylene-blue is heated with sulphuric acid, is isolated as the *hydriodide*,

$$[NMe_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{N}{S\text{-}}>C_6H_2(OH)\colon NH_2I]_2HI,$$

which is obtained as an olive-green, crystalline powder. It forms blue solutions with a slight red fluorescence, dyes silk and mordanted cotton a more violet shade than methylene-blue, is decolorised by stannous chloride, and forms precipitates with ammonia, mercuric chloride, and potassium dichromate.

The action of bromine on methylene-blue hydrochloride in glacial acetic acid solution leads to the formation of a *product* which crystallises in brownish-violet needles, and has solubilities and gives colorations resembling those of methylene-blue.

Dinitromethylthionine, formed by the action of nitric acid on methylene-blue or methylene-green in hot acetic acid solution, is isolated as the *nitrate*, $NMe_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{N}{S\text{-}}>C_6H(NO_2)_2\colon NH_2\cdot NO_3$, which crystallises in olive-brown needles, and detonates at about 240°. The *hydrobromide* crystallises in olive-brown needles. The dye-salts form bluish-red, dichroic solutions in methyl or ethyl alcohol, acetic acid, or acetone with scarlet fluorescence; the similarly coloured aqueous solution is not fluorescent. Addition of ammonia to the aqueous solution precipitates the brown, amorphous base, which detonates when heated, and remains partly unchanged when boiled with acetic acid. The dinitro-compound dyes silk or mordanted cotton a brownish-violet.

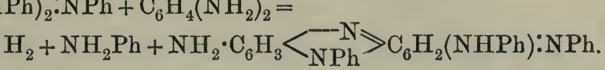
Reduction of the dinitro-nitrate with zinc dust and glacial acetic acid leads to the formation of a soluble *leuco-base*, which is readily oxidised by ferric chloride, forming *diaminodimethylthionine*. The *hydrobromide* of this is a bluish-black, amorphous powder, forms bluish-green solutions, and dyes silk and mordanted cotton green.

The absorption spectra of the various compounds are described, and also the colorations given with strong acids. G. Y.

Synthesis of Phenylated *s*-Anilinophenosafranine. Philippe Barbier and Paul Sisley (*Compt. rend.*, 1907, **145**, 1185—1187. Compare Abstr., 1905, i, 840; 1906, i, 51, 989; 1907, i, 160, 563).—

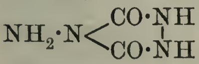
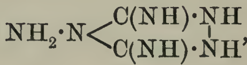
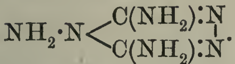
When a mixture of azophenine (Fischer and Hepp, Abstr., 1903, i, 134) and *p*-phenylenediamine in molecular proportions is heated in alcohol at 165° during six to seven hours, aniline is produced together with a *phenylated* s-*anilinophenosafranine*, which can be separated as its *hydrochloride*, $C_{30}H_{23}N_5,2HCl$, a dark crystalline powder with a feeble metallic reflex; the *platinichloride*, $C_{30}H_{23}N_5,H_2PtCl_6$, is a reddish-brown powder. It dyes mordanted silk or cotton a beautiful violet-blue shade. The mechanism of the reaction, and the constitution of the new dye, are represented in the following scheme:

$NPh\colon C_6H_2(NHPh)_2\colon NPh + C_6H_4(NH_2)_2 =$

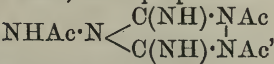


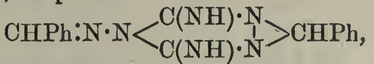
$$H_2 + NH_2Ph + NH_2\cdot C_6H_3<\begin{array}{c}N\\ NPh\end{array}>C_6H_2(NHPh)\colon NPh.$$

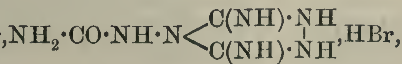
If in the above reaction the *p*-phenylenediamine is replaced by *as*-dimethyl- or diethyl-*p*-phenylenediamine, soluble dyes are obtained in which the NH_2-group of the original compound is replaced by NMe_2 or NEt_2, and these dye in a bluer shade. M. A. W.

Action of Cyanogen Bromide on Hydrazine. *N*-Aminoguanazole (Guanazine). III. GUIDO PELLIZZARI and ANGELO REPETTO (*Gazzetta*, 1907, **37**, ii, 317—326. Compare Abstr., 1907, i, 833).—The hexagonal formula for guanazine (Abstr., 1905, i, 577) was based on the analogy of this compound with urazine and thiourazine. Now that urazine has been shown to have the structure:  $NH_2\cdot N<\begin{array}{l}CO\cdot NH\\ CO\cdot NH\end{array}$ (Busch, Abstr., 1901, i, 488; Stollé, Abstr., 1907, i, 654), guanazine must be 4-aminoguanazole,  $NH_2\cdot N<\begin{array}{l}C(NH)\cdot NH\\ C(NH)\cdot NH\end{array}$, or  $NH_2\cdot N<\begin{array}{l}C(NH_2)\colon N\\ C(NH_2)\colon N\end{array}$. This structure is in accord with the properties and reactions of the compound (compare Pellizzari and Roncagliolo, Abstr., 1901, i, 772).

4-Aminoguanazole (guanazine), $C_2N_6H_6$, separated from its hydrobromide, separates from water in large, faintly yellow crystals, or from alcohol in minute, almost white crystals, m. p. 257° (decomp.), has a marked alkaline reaction, and reduces ammoniacal silver nitrate and Fehling's solution on heating. Its *nitrate*, $C_2N_6H_6,HNO_3$, m. p. 210°; *sulphate*, $(C_2N_6H_6)_2,H_2SO_4,H_2O$, m. p. 275°, and *acetate*, $C_2N_6H_6,C_2H_4O_2,1\frac{1}{2}H_2O$, m. p. 175°, were prepared.

Triacetylaminoguanazole,  $NHAc\cdot N<\begin{array}{l}C(NH)\cdot NAc\\ C(NH)\cdot NAc\end{array}$, crystallises from alcohol in shining, white needles, m. p. 240°.

Dibenzylideneaminoguanazole,  $CHPh\colon N\cdot N<\begin{array}{l}C(NH)\cdot N\\ C(NH)\cdot N\end{array}>CHPh$, prepared by the interaction of aminoguanazole and benzaldehyde in alcoholic solution in presence of piperidine, separates from alcohol in intensely yellow crystals, m. p. 196°. Its *hydrochloride*, $C_{16}N_6H_{14},HCl$, was prepared.

Carbamidoguanazole hydrobromide,  $NH_2\cdot CO\cdot NH\cdot N<\begin{array}{l}C(NH)\cdot NH\\ C(NH)\cdot NH\end{array},HBr$,

prepared by the interaction of aminoguanazole hydrobromide, potassium cyanate, and hydrobromic acid, has m. p. 221°. The free base decomposes readily, and could not be isolated. T. H. P.

Formation of Pyrimidine Derivatives from Purine Bases.

HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, 53, 508—513).—Several of Burian's experiments on heating guanine and adenine with sulphuric acid and sucrose (Abstr., 1907, i, 735) have been repeated, but in no case has any pyrimidine derivative been obtained.

J. J. S.

The Relation between Quinonehydrazones and *p*-Hydroxyazo-compounds. IV. Condensation of Nitro-derivatives of Phenylhydrazine with Quinones and Quinoneoximes of the Benzene Series.

WALTHER BORSCHE (*Annalen*, 1907, 357, 171—191. Compare Abstr., 1904, i, 1056; 1905, i, 719; 1906, i, 319).—Attempts to prepare *p*-hydroxyazo-compounds of the benzene series by the method employed by Zincke in the naphthalene series have hitherto been unsuccessful. The results obtained (Abstr., 1905, i, 719) with acylhydrazides suggested that phenylhydrazines containing negative substituting groups might react with benzoquinones. This has now been found to be the case with *o*-nitrophenylhydrazine, which reacts with benzoquinones and their oximes, forming *p*-hydroxyazo-compounds of the type: $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH$, which are identical with the substances obtained by coupling diazotised *o*-nitroaniline with phenols, and quinoneoximehydrazones, which are considered to be of the type: $NO_2 \cdot C_6H_4 \cdot NH \cdot N{:}C_6H_4{:}NOH$, respectively. *p*-Nitrophenylhydrazine, on the other hand, reacts only with the quinoneoximes, whilst *m*-nitrophenylhydrazine does not form either hydroxyazo-compounds or quinoneoximehydrazones. 2:4-Dinitrophenylhydrazine reacts with quinones and quinoneoximes more readily than does *o*-nitrophenylhydrazine, but attempts to form hydroxyazo-compounds from 2:4:6-trinitrophenylhydrazine have so far been unsuccessful.

1:3-*Bis-2′-nitrobenzeneazo-4-hydroxybenzene*, $OH \cdot C_6H_3(N_2 \cdot C_6H_4 \cdot NO_2)_2$, is formed together with 4-hydroxybenzeneazo-2′-nitrobenzene by Elb's and Keiper's method (Abstr., 1903, i, 662); it crystallises from glacial acetic acid in dark brown needles, m. p. 203°.

2′-*Nitro-4-hydroxy-3-methylazobenzene*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3Me \cdot OH$, obtained in orange-red, crystalline nodules, m. p. 111—112°, prepared from toluquinone and *o*-nitrophenylhydrazine hydrochloride, or, together with *bis*-o-*nitrobenzeneazo*-o-*cresol*, crystallising in dark brown needles, m. p. 258—260° evolving gas, by the action of diazotised *o*-nitroaniline on *o*-cresol.

2′-*Nitro-4-hydroxy-2-methyl-5*-iso*propylazobenzene*,

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2MePr^{\beta} \cdot OH,$$

crystallising in long needles, m. p. 144—145°, is prepared from thymoquinone and *o*-nitrophenylhydrazine, or, together with a small amount of the corresponding *bisazo*-compound, crystallising in blackish-brown needles, m. p. 179—180° (decomp.), from diazotised *o*-nitroaniline and thymol.

2′ : 4′-*Dinitro-4-hydroxyazobenzene*, $OH\cdot C_6H_4\cdot N_2\cdot C_6H_3(NO_2)_2$, crystallising in brown needles, m. p. 185—186°; 2′ : 4′*dinitro-4-hydroxy-3-methylazobenzene*, $OH\cdot C_6H_3Me\cdot N_2\cdot C_6H_3(NO_2)_2$, forming an orange powder, m. p. 127—128°, and 2′ : 4-*dinitro-4-hydroxy-2-methyl*-5-iso-*propylazobenzene*, $OH\cdot C_6H_2MePr^{\beta}\cdot N_2\cdot C_6H_3(NO_2)_2$, crystallising in dark red needles, m p. 179—180°, are prepared by the action of 2 : 4-dinitrophenylhydrazine on quinone, toluquinone, and thymoquinone respectively, and form bluish-red to violet-blue solutions in dilute alkalis.

Benzoquinoneoxime-o-*nitrophenylhydrazone*, $C_{12}H_{10}O_3N_4$, prepared by the action of *o*-nitrophenylhydrazine on benzoquinoneoxime in cooled alcoholic solution, crystallises in dark red needles, and gradually decomposes when heated. The *benzoyl* derivative,

$$NO_2\cdot C_6H_4\cdot NH\cdot N\colon C_6H_4\colon N\cdot OBz,$$

formed from benzoquinoneoxime benzoate, is obtained as an insoluble, scarlet precipitate, and does not melt in a sulphuric acid bath. When heated with glacial acetic acid, or more rapidly when treated with chromic or concentrated nitric acid in glacial acetic acid solution, benzoquinoneoxime-2-nitrophenylhydrazone is converted into 4 : 4′-*bis*-o-*nitrobenzeneazoazoxybenzene*, $ON_2(C_6H_4\cdot N_2\cdot C_6H_4\cdot NO_2)_2$, which is formed also as a by-product in the preparation of the hydrazone, or by the action of benzaldehyde on the hydrazone. It crystallises in dark yellow needles, m. p. 258° (decomp.). The action of nitric acid on benzoquinoneoxime-*o*-nitrophenylhydrazone in boiling glacial acetic acid solution, or of hydrogen peroxide on the hydrazone in dilute sodium hydroxide solution, leads to the formation of 2 : 4′-*dinitroazobenzene*, $C_{12}H_8O_4N_4$, which crystallises in iridescent leaflets, m. p. 131—132°.

Toluquinone-2-*oxime*-5-o-*nitrophenylhydrazone*,

$$NO_2\cdot C_6H_4\cdot NH\cdot N\colon C_6H_3Me\colon NOH,$$

prepared from nitroso-*m*-cresol and *o*-nitrophenylhydrazine hydrochloride, is obtained as a dark brown, flocculent precipitate, m. p. 206—207° (decomp.), and when treated with nitric acid in boiling glacial acetic acid solution yields 2 : 4′-*dinitro-3′-methylazobenzene*, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3Me\cdot NO_2$, crystallising in dark yellow leaflets, m. p. 128°.

Thymoquinone-2-*oxime*-5-o-*nitrophenylhydrazone*,

$$NO_2\cdot C_6H_4\cdot NH\cdot N\colon C_6H_2MePr^{\beta}\colon NOH,$$

prepared from nitrosothymol, crystallises in dark red needles, m. p. 218—220° (decomp.).

The condensation products of *p*-nitrophenylhydrazine and quinoneoximes are unstable. Only the more easily isolated *benzoylbenzoquinoneoxime*-p-*nitrophenylhydrazone*,

$$NO_2\cdot C_6H_4\cdot NH\cdot N\colon C_6H_4\colon N\cdot OBz,$$

is described. It is formed from benzoquinoneoxime benzoate, crystallises in small, reddish-brown leaflets, does not melt at 260°, and is insoluble in the usual organic solvents.

Benzoquinoneoxime-2 : 4-*dinitrophenylhydrazone*,

$$C_6H_3(NO_2)_2\cdot NH\cdot N\colon C_6H_4\colon NOH,$$

forms a dark red, crystalline powder, m. p. 214—215° (decomp.), dissolves to a reddish-blue solution in dilute sodium hydroxide, and when boiled with glacial acetic acid yields 2:4:4′-trinitroazobenzene.

*Toluquinone-2-oxime-5-*o : p-*dinitrophenylhydrazone*,
$C_6H_3(NO_2)_2 \cdot NH \cdot N{:}C_6H_3Me{:}NOH$,
forms a glistening, bluish-red powder, decomp. 222—223°, and when treated with nitric acid in hot glacial acetic acid solution yields 4 : 2′ : 4′-*trinitro-3-methylazobenzene*, $C_6H_3(NO_2)_2 \cdot N_2 \cdot C_6H_3Me \cdot NO_2$, crystallising in reddish-brown needles, m. p. 164—165°.

*Thymoquinone-2-oxime-5-*o : p-*dinitrophenylhydrazine*,
$C_6H_3(NO_2)_2 \cdot NH \cdot N{:}C_6H_2MePr^{\beta}{:}NOH$,
crystallises in dark red needles, decomp. 249—250°. 4 : 2′ : 4′-*Trinitro-3-methyl-6-*iso*propylazobenzene*, $C_6H_3(NO_2)_2 \cdot N_2 \cdot C_6H_2MePr^{\beta} \cdot NO_2$, crystallises in yellowish-red needles, m. p. 198°. G. Y.

Azo-derivatives of Guaiacol. Amedeo Colombano and Battista Leonardi (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 639—648; *Gazzetta*, 1907, **37**, 461—471. Compare Colombano, Abstr., 1907, i, 1091).—The compounds not already described (*loc. cit.*) are as follows.

The *acetyl* derivative of *benzeneazoguaiacol*, $C_{15}H_{14}O_3N_2$, separates from light petroleum in reddish-brown, acicular crystals, m. p. 61°.

The *ethyl ether* of *benzeneazoguaiacol*, $C_{15}H_{16}O_2N_2$, crystallises from alcohol or water in tufts of long, silky needles, m. p. 86—89°.

o-*Nitrobenzeneazoguaiacol*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot OMe$, separates from aqueous alcohol in red, acicular crystals, m. p. 144°.

m-*Nitrobenzeneazoguaiacol*, $C_{13}H_{11}O_4N_3$, crystallises from aqueous alcohol in yellowish-red needles, m. p. 124°. Its *acetyl* derivative, $C_{15}H_{13}O_5N_3$, has m. p. 95—97°.

p-*Nitrobenzeneazoguaiacol*, $C_{13}H_{11}O_4N_3$, separates from aqueous alcohol in chocolate-brown needles, m. p. 125—135°.

o-*Tolueneazoguaiacol*, $C_6H_4Me \cdot N_2 \cdot C_6H_3(OH) \cdot OMe$, separates in reddish-brown, acicular crystals, m. p. 85°. Its *acetyl* derivative, $C_{16}H_{16}O_3N_2$, forms orange-red rhombohedra, m. p. 87°.

a-Naphthylazoguaiacol, $C_{10}H_7 \cdot N_2 \cdot C_6H_3(OH) \cdot OMe$, forms brownish-black needles, m. p. 125°. Its *acetyl* derivative, $C_{19}H_{16}O_3N_2$, forms dark orange-red, acicular crystals, m. p. 105—110°.

β-Naphthylazoguaiacol, $C_{17}H_{14}O_2N_2$, separates from aqueous alcohol in pale yellow, flocculent crystals, m. p. 92—94°. T. H. P.

Action of Thorium Nitrate and of Uranyl Nitrate on Albumins. Béla Szilard (*J. Chim. phys.*, 1907, **5**, 495—496).—When the albumin of white of egg, coagulated by boiling, is added in small quantities at a time to a boiling 2% aqueous solution of thorium or uranyl nitrate, a considerable amount of it goes into solution, leaving only a slight insoluble residue. The filtered thorium solution is colourless and slightly opalescent, and does not give the ordinary reactions for thorium or for albumin; the latter seems to be present as an albumose or peptone. The uranyl solution is yellow in colour. Keratin is dissolved by these salt solutions in a similar way. G. S.

Conditions of Hydrolysis of Protoplasmides. Alexandre Étard and Antony Vila (*Compt. rend.*, 1907, **145**, 1217—1219. Compare Abstr., 1901, i, 490; ii, 563; 1902, i, 110, 589).—The author discusses the unsatisfactory nature of the present methods of hydrolysing protoplasmides and the impossibility of obtaining quantitative results. The hydrolysis is usually effected by means of excess of acids or bases, and the salts formed when they are neutralised carry down a large proportion of the products of hydrolysis. Thus 1 kilo. of beef muscle after removal of the fat and drying at 100° yielded 240 grams of dry muscular tissue; this was hydrolysed by means of 650 grams of sulphuric acid in 1200 grams of water, and neutralised with baryta; it yielded 171 grams of dry hydrolytic products, 15 grams being retained by the barium sulphate. M. A. W.

Hydrolysis of Hordein. A. Kleinschmitt (*Zeitsch. physiol. Chem.*, 1907, **54**, 110—118).—By hydrolysis of hordein (from barley) by concentrated hydrochloric acid, the following percentage yields were obtained: alanine 1·34, aminovaleric acid 1·40, leucine 7·00, pyrrolidine-2-carboxylic acid (α-proline) 5·88, phenylalanine 5·48, glutamic acid 41·32, aspartic acid 1·32, serine 0·10, histidine 0·51, arginine 3·14, tyrosine 4·00, ammonia 4·34, leucineimide 0·58. Like zein and gliadin (the other alcohol-soluble vegetable proteins), hordein contains no glycine and no lysine. As shown by the results of hydrolysis, gliadin and hordein are not identical, as has sometimes been supposed.
G. B.

Urochrome. Ottorino Bocchi (*Beitr. chem. Physiol. Path.*, 1907, **11**, 79—80).—A method for preparing urochrome is given, and is said to yield a purer product than that obtained according to Garrod's method. The urochrome is obtained free from indican and urea.
G. B.

Nucleo-protein of the Placenta. M. Savarè (*Beitr. chem. Physiol. Path.*, 1907, **11**, 73—75).—The nucleo-protein of the placenta contains C, 50%; H, 7·3%; N, 15%; S, 1%, and P, 0·45%. In its composition, and especially in its low phosphorus content, it shows a certain analogy to the nucleo-protein of the lacteal gland; this is possibly connected with the fact that both organs are concerned in infantile nutrition.
G. B.

Polypeptidephosphoric Acid (Paranucleic Acid) from Caseinogen. Alfred Reh (*Beitr. chem. Physiol. Path.*, 1907, **11**, 1—18).—The paranucleic acid of Salkowski was prepared from a caseinogen solution which had undergone peptic digestion for two days by precipitation with uranyl acetate in the presence of acetic acid. The uranyl compound is readily soluble in hydrochloric acid; its phosphorus is removed quantitatively by boiling baryta, and it does not contain sulphur; phosphorus and uranium are present in atomic proportions. The free acid contains P 6·9%, or eight times as much as that of the caseinogen employed (Salkowski's preparation contained 4·3% P).

The uranyl compound was hydrolysed by boiling with 25% sulphuric acid, and yielded arginine, histidine, lysine, alanine, proline, aminovaleric acid, leucine, *iso*leucine, phenylalanine, tyrosine, aspartic acid, and glutamic acid. G. B.

Nucleic Acids in Animals. OSWALD SCHMIEDEBERG (*Arch. exp. Path. Pharm.*, 1907, **57**, 309—337).—The empirical formula for nucleic acid reckoned from elementary analysis is $C_{40}H_{56}N_{14}O_{16},2P_2O_5$. A distinction is drawn between this, the anhydrous form of the acid, and the hydrated form, which has $2H_2O$ (or, in a few cases, $5H_2O$) in addition. The anhydrous form possesses the property of gelatinising. The preparations were made from salmon-roe, thymus, pancreas, and thyroid. The bulk of the paper relates to the method used in preparing the substance; the separation by means of its copper salt was mainly used. W. D. H.

Guanylic Acid from the Pancreas. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, **53**, 539—544).—It is shown that guanylic acid can be prepared from the nucleo-protein of the pancreas by Bang's method (Abstr., 1899, i, 179; 1901, i, 299; Fürth and Jerusalem, Abstr., 1907, i, 993), and a nucleic acid by Neumann's method. Guanylic acid does not yield glycerol on hydrolysis. J. J. S.

Guanylic Acid. IVAR BANG (*Beitr. chem. Physiol. Path.*, 1907, **11**, 76—78).—A reply to von Fürth and Jerusalem (Abstr., 1907, i, 993), who refuse to place this acid apart from other nucleic acids. These authors did not work with pure material. The large nitrogen deficit in their determination of the purine bases was due to faulty application of the method, and led to great loss, especially as regards the guanine. Further work is promised. G. B.

The Compound of Uric Acid with Nucleic Acid. Y. SEO (*Arch. expt. Path. Pharm.*, 1907, **58**, 75—92).—This compound, described by Minkowski and by Goto (Abstr., 1900, ii, 421, 740), was prepared by dissolving nucleic acid and uric acid in dilute sodium hydroxide, acidifying with acetic acid, filtering off the excess of uric acid, which separated after a time, and finally precipitating the compound by adding concentrated hydrochloric acid to the filtrate. The amorphous, colourless precipitate gives the murexide reaction; its solution in water does not yield a precipitate with acetic acid or with silver nitrate. When boiled with acetic acid, or treated with excess of ammonia in the cold, it is decomposed into its two components. Analysis of the copper compound indicates that 2 molecules of nucleic acid are combined with 1 of uric acid.

Egg-albumin precipitates nucleic acid from the combination of the two acids, thus setting the uric acid free; the latter can be obtained crystalline from the albumin filtrate. Hence uric acid may occur as a nucleic acid compound in the blood, despite the fact that free uric acid is obtained after removal of the proteins by acidification and boiling.

After the injection of uric acid + nucleic acid, much more uric acid is found in the urine than when the two substances are injected at separate times (compare Abstr., 1906, ii, 109). G. B.

Neurokeratin. ALFRED ARGIRIS (*Zeitsch. physiol. Chem.*, 1907, **54**, 86—94).—The method of preparation (from human brains) is described in detail, and is a modification of that used by Kühne and Chittenden. The composition of the substance agrees closely with that found by the latter authors as regard C, H, and N, but somewhat higher values for S were found (2·24—2·31%, instead of 1·75%). On hydrolysis, by boiling with 33% sulphuric acid, neurokeratin yielded: lysine, 2·72%; arginine, 2·28%; histidine, 0·76%; tyrosine, 4·60%, and cystine, 1·50%, besides other amino-acids. G. B.

Separation of Proteins. II. Deutero-albumose. Henry C. Haslam (*J. Physiol.*, 1907, **36**, 164—176. Compare Abstr., 1905, i, 495).—Deutero-albumose is resolved by alcohol into two substances differing in solubility, but it is not decomposed by ammonium or zinc sulphate. The total number of the albumoses of Witte's peptone is reduced to five, namely, hetero-proteose, two varieties of proto-proteose, and two of deutero-proteose. W. D. H.

Compounds of Protamines with other Proteins. Andrew Hunter (*Zeitsch. physiol. Chem.*, 1907, **53**, 526—538. Compare Kossel, *Deut. Med. Woch.*, 1894, No. 7).—Clupein yields precipitates with faintly ammoniacal solutions of crystallised egg-albumin, casein, hemielastin, gelatin, edestin, hetero-albumose, and proto-albumose. Precipitates are not obtained with elastin, peptone, deutero-albumose, histopeptone, and various polypeptides. A solution of metaprotein in a slight excess of sodium hydroxide and a solution of histone sulphate in sodium carbonate yield precipitates.

The following figures give the number of parts by weight of the protein which unite with one part by weight of clupein: ovalbumin, 4·1; gelatin, 4·8; hemielastin, 5·2; casein, 2·5; edestin, 8·5. J. J. S.

Pepsin and Chymosin (Rennin). J. W. A. Gewin (*Zeitsch. physiol. Chem.*, 1907, **54**, 32—79).—Bang's parachymosin, obtained from the pig's stomach, is not essentially different from the chymosin from the calf. Such differences as exist between the two preparations are due to admixed impurities.

Attempts to separate rennin from pepsin by means of dialysis, the addition of much protein, &c., were unsuccessful. In the researches of those observers (Bang, Schmidt-Nielsen) who obtained enzyme solutions having only a peptic or only a rennitic action, the action of the other enzyme was only inhibited, and could be restored by removal of the inhibiting substance. Pepsin and rennin are one and the same ferment. The rennet action is the first stage in the digestion of caseinogen; if hydrogen ions are absent and calcium ions are present, the digestion stops and a curd separates; if a sufficient number of hydrogen ions are present, ordinary peptic digestion proceeds. G. B.

Method for the Determination of the Accelerating Action of Sodium and Potassium Salts on the Coagulation of Milk by Ferments. C. Gerber (*Compt. rend.*, 1907, **145**, 831—833. Compare Abstr., 1907, i, 1100).—The author recommends that the milk used in the determination of the accelerating influence of certain salts on coagulation should be treated previously with sodium oxalate, in order to eliminate the action of the calcium compounds present naturally in the milk. These compounds interfere with the action of such salts as fluorides, the calcium combining with the fluorine and causing untrustworthy results to be obtained. W. P. S.

Peroxydases from Beetroot. ADOLF ERNEST and HEINRICH BERGER (*Ber.*, 1907, 40, 4671—4679. Compare Bach and Chodat, Abstr., 1902, ii, 344, 522; 1903, i, 377, 378; 1904, i, 542).—The beetroot is extracted with diluted alcohol, and an aqueous solution of the raw material so obtained treated with a mixture of absolute alcohol and ether. The precipitated material consists of peroxydases only, and does not contain any oxydase, catalase, amylase, invertase, emulsin, or proteolytic enzyme.

The quantity of purpurogallin produced by the action of the peroxydases on a mixture of pyrogallol and hydrogen peroxide increases with an increase in the proportion of hydrogen peroxide or peroxydase, but decreases with an increase in the proportion of pyrogallol.

W. H. G.

Philothion. JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1907, [iv], 1, 1051—1053. Compare Abstr., 1907, i, 372).—It is shown that the white of a duck's egg furnishes but little hydrogen sulphide when mixed with sulphur, and cannot therefore be used as a source of philothion.

The reciprocal action of oxidising ferments and philothion, simultaneously present in muscular tissue, has been examined by extracting finely-divided cock's muscle with a dilute aqueous solution of sodium fluoride and potassium iodide, the latter being a solvent for oxydases. This solution contains philothion when freshly made, but after being kept at 40—45° during five hours it no longer gives the characteristic philothion reaction, although it still contains albumin. This disappearance of philothion (albumin hydride) it is suggested is due to dehydrogenation by the action of the oxydases (*loc. cit.*).

Since the soluble albumin of the circulatory system is free from philothion whilst that of muscular tissue contains it, it must be assumed that the living cell has the property of hydrogenating albumin, which can then be reoxidised to simple albumin by other constituents of muscular tissue. Philothion therefore plays the part of a hydrogenating enzyme. T. A. H.

Organic Chemistry.

Viscosity of Ethyl Alcohol. L. Gaillard (*J. Pharm. Chim.*, 1907, [vi], 26, 481—487).—The relative viscosities (compared with that of water taken as unity) of absolute ethyl alcohol and of mixtures containing from 1 to 10 molecules of water per molecule of alcohol are 1·45, 2·53, 2·96, 3·10, 3·10, 2·95, 2·84, 2·67, 2·55, 2·43, and 2·23 respectively, whilst those of mixtures containing 95%, 20%, 15%, 11%, 10%, and 5% of alcohol are 1·78, 1·96, 1·65, 1·45, 1·35, and 1·21, all the values having been obtained at 15°. Examination of these values shows that the viscosity of ethyl alcohol increases with dilution until a maximum value of 3·1 is reached for the two mixtures of the composition $EtOH,3H_2O$ and $EtOH,4H_2O$, and then diminishes, and that absolute alcohol and a mixture containing 11% of alcohol have the same viscosity. This confirms the existence of the trihydrate, the formation of which is accompanied by the maximum contraction, and renders probable the existence of the tetrahydrate. Mixtures of the two alcohols $EtOH,3H_2O$ and $EtOH,4H_2O$ in any proportion whatever all have the viscosity 3·1, indicating that intermediate hydrates are not formed. E. H.

Action of Zinc Allyl Iodide on the Anhydrides of Monobasic Acids. Alexander M. Saytzeff (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, *Chem.*, 1232—1239).—When an anhydride of a monobasic acid reacts with allyl iodide in the presence of zinc, the following reactions most probably occur: $O(CO{\cdot}R)_2 + C_3H_5{\cdot}ZnI = C_3H_5{\cdot}CR(OZnI){\cdot}O{\cdot}COR \longrightarrow CR(C_3H_5)_2{\cdot}OH$, and, as a side reaction, $CR(C_3H_5)_2{\cdot}OZnI \longrightarrow$

$$C_3H_5{\cdot}CR{\cdot}O{\cdot}COR.$$

The yield and purity of the alcohol are much superior to that obtained when the ester is employed instead of the anhydride. The following substances have been obtained. Methyldiallylcarbinol, yield 36·5% of the theoretical, having b. p. 157—159°, D_0^0 0·87747, D_0^{20} 0·86314, D_{20}^{20} 0·86258 (Sorokin gives D_0^0 0·8640, D_0^{13} 0·8524). Ethyldiallylcarbinol, yield 37—39%, b. p. 175—176°/755·6 mm., D_0^0 0·88603, D_0^{20} 0·86877, D_{20}^{20} 0·87002 (Smirensky: D_0^0 0·8776, D_0^{17} 0·8637). Propyldiallylcarbinol, yield nearly 41%, b. p. 192—194°, D_0^0 0·87939, D_0^{20} 0·86286, D_{20}^{20} 0·86412 (P. and A. Saytzeff: D_0^0 0·8707, D_0^{20} 0·8564). *iso*Propyldiallylcarbinol, yield 37%, b. p. 187—188°, D_0^0 0·88859, D_0^{20} 0·87133, D_{20}^{20} 0·87259 (Rjabinin and Saytzeff: D_0^0 0·8647, D_0^0 0·8512). Z. K.

Alkylene Glycol-chlorohydrin Ethers and their Changes. Josef Houben and Karl Führer (*Ber.*, 1907, 40, 4990—5000).—Ethylene glycolchlorohydrin ether [α-chloro-β-ethoxybutane], $CH_2Cl{\cdot}CHEt{\cdot}OEt$, originally obtained by Lieben, using zinc ethyl, is more conveniently prepared by the interaction of dichloro-ether and magnesium ethyl bromide. It is not converted into methyl ethyl ketone or, indeed, changed by heating in boiling methyl alcohol with sodium hydroxide. *α-Chloro-β-ethoxy*iso*hexane*, $CH_2Cl{\cdot}CH(C_4H_9){\cdot}OEt$, is a colourless liquid, b. p. 60—61°/8 mm.

iso-α-*Chloro-β-ethoxy*-iso*heptane*, $CH_2Cl·CH(C_5H_{11})·OEt$, is a colourless liquid of unpleasant odour, b. p. 77—78°/9 mm. *β-Chloro-α-ethoxyethylbenzene*, $CH_2Cl·CHPh·OEt$, is a colourless, pleasant smelling liquid, b. p. 107—108°/9 mm.; when heated with sodium hydroxide, it is converted almost quantitatively into acetophenone, and for the preparation of this from bromobenzene it is not necessary to first purify the hydrin ether. By the action of sodium iodide on the above chlorohydrin ether, the chlorine is to a large extent replaced by iodine; the product obtained has b. p. 110—111°/9·5 mm., and distils as a dark red oil without much decomposition at 226°/760 mm. *γ-Chloro-α-ethoxypropylbenzene*, $CH_2Cl·CH(CH_2Ph)·OEt$, is a colourless liquid of agreeable odour, b. p. 125—126°/9·5 mm., which, like the aliphatic compounds, is not altered on boiling with sodium hydroxide. 1-*β-Chloro-α-ethoxyethylnaphthalene*, $CH_2Cl·CH(C_{10}H_7)·OEt$, has b. p. 178—179°/9 mm., and forms a yellow liquid of faint odour. Heated with sodium hydroxide, it forms α-naphthyl methyl ketone. E. F. A.

Oxidation of Butyric Acid by Hydrogen Peroxide. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 77—89).—Ammonium butyrate is readily oxidised by hydrogen peroxide at 37°, but the reaction is accelerated by warming. The products obtained were: acetoacetic acid, acetone, propaldehyde, acetaldehyde, acetic and formic acids, and carbon dioxide; propionic acid was probably also present. It is probable that α- and β-hydroxybutyric acids are the initial products. All products except acetone are on further treatment converted eventually with carbon dioxide and water. Acetone is very resistant to hydrogen peroxide. There is no need to assume that acetone is formed as an intermediate substance in the oxidation of all the butyric acid formed in the body. It is probable that β-hydroxybutyric acid may be decomposed so as to give acetic acid and its oxidation products. It is much less probable that the α-acid is an alternative initial product in tissue oxidation; this, however, may be further oxidised through propionic acid. W. D. H.

Mercuric Heptoate. J. TH. BORNWATER (*Rec. trav. chim.*, 1907, 26, 413).—When yellow mercuric oxide is shaken with an aqueous solution of *n*-heptoic acid, at the end of some days the oxide is completely transformed into a white precipitate of *mercuric heptoate*, $(CH_2Me·[CH_2]_4·CO_2)_2Hg$. It crystallises from methyl alcohol in nacreous plates, m. p. 106·5°. Solutions of the salt decompose after a time, mercuric oxide being deposited; they are rendered more stable by addition of heptoic acid. Mercuric heptoate does not form a double salt with mercuric chloride. E. H.

Derivatives of Undecenoic Acid. J. TH. BORNWATER (*Rec. trav. chim.*, 1907, 26, 409—412).—Methyl undecenoate (Noerdlinger, Abstr., 1890, 1237), prepared according to Perkin's method for the ethyl ester (Trans., 1886, 49, 206), has b. p. 249·5—250°/780 mm., m. p. $-27·5°$, D^{15} 0·889. As the temperature rises from 11·2° to 25°, the n_D falls from 1·44301 to 1·43727. Ethyl undecenoate has m. p. $-37·5°$, b. p. 263—263·5°/780 mm., D^{15} 0·881. *Undecenomethylamide*,

$CH_2:CH·[CH_2]_8·CO·NHMe$,

prepared by the action of an aqueous solution of methylamine on the crude chloride, forms fine, crystalline plates, m. p. 46° (below that of the amide, Franchimont, Abstr., 1897, ii, 542). *Undecenodimethylamide*, $CH_2\colon CH\cdot[CH_2]_8\cdot CO\cdot NMe_2$, obtained by shaking an ethereal solution of the chloride with an aqueous solution of dimethylamine hydrochloride, is a liquid, b. p. 186·5°/20 mm., D_4^{18} 0·89278, which solidifies when cooled in ice and salt to a solid, m. p. −16·5°.

E. H.

Action of Ozone on Compounds containing Triple Linkings. Carl D. Harries (*Ber.*, 1907, **40**, 4905—4908).—The author disputes Molinari's statement (Abstr., 1907, i, 1039) that ozone does not react with substances containing a triple linking or a benzene double linking. Stearolic acid and phenylpropiolic acid yield with ozone unstable substances which exhibit the typical reactions of ozonides.

C. S.

Oxidation of Ammonium Salts of Hydroxy-fatty Acids with Hydrogen Peroxide. Henry D. Dakin (*J. Biol. Chem.*, 1908, **4**, 91—100).—The ammonium salts of glycollic, lactic, α- and β-hydroxybutyric, α-hydroxy*iso*butyric, and α-hydroxy*iso*valeric acids were oxidised with hydrogen peroxide. With the exception of glycollic and β-hydroxybutyric acids, the primary products are an aldehyde, carbon dioxide, and water:

$$[R\cdot CH(OH)\cdot CO_2H = R\cdot CHO + CO_2 + H_2O].$$

In the case of α-hydroxy*iso*butyric acid, acetone is formed. More or less of the aldehyde is further oxidised to the corresponding acid, and in some cases oxidation goes on still further; thus lactic acid yields acetaldehyde, acetic acid, and carbon dioxide. Leucic acid undergoes oxidation like other hydroxy-acids. Glycollic acid yields first glyoxylic acid and formaldehyde, then formic acid, and, finally, carbon dioxide and water. β-Hydroxybutyric acid yields numerous products, including acetoacetic acid, acetone, acetaldehyde, acetic and formic acids, and carbon dioxide. W. D. H.

The Reduction of Ethyl Oxalate. Wilhelm Traube (*Ber.*, 1907, **40**, 4942—4956. Compare Löwig, *J. pr. Chem.*, 1861, [i], **83**, 129, and **84**, 1; Debus, this Journ., 1872, **25**, 365; Eghis, *ibid.*, 1871, **24**, 820).—A solution of ethyl oxalate in absolute alcohol was reduced with sodium amalgam, and, in order to avoid hydrolysis of the esters, the product was mixed with an excess of alcoholic hydrogen chloride and fractionally distilled. In the first fraction, ethyl alcohol, hydrogen chloride, and a small amount of ethyl carbonate passed over, and then a small amount of ethyl glyoxalate alcoholate and ethyl glycollate. A fraction, distilling between 170° and 220°, consisted mainly of ethyl diethylglyoxylate, $CH(OEt)_2\cdot CO_2Et$, and ethyl oxomalonate, $CO(CO_2Et)_2$, together with a little ethyl oxalate. The residue when distilled under reduced pressure gave a fraction 160—200°/20 mm., consisting mainly of ethyl deoxalate (Klein, Abstr., 1880, 36) (crystals) and ethyl tartrate (liquid). The diethylglyoxylic ester, which is formed in considerable amounts, is not a primary reduction product, but is formed by the action of the alcohol and hydrogen chloride on the ethyl glyoxylate alcoholate. The formation of the acetal can be prevented by using just sufficient hydrogen chloride to neutralise the alkali formed during the reduction, or by using an alcoholic solution of oxalic acid. Under these conditions, the chief product is the alcoholate (20—25 grams from 100 of ethyl oxalate), which appears to be the first product of reduction : $EtO·CO·CO·OEt \longrightarrow EtO·CO·CH(OH)·OEt$. *Ethyl glyoxalate alcoholate*, $CO_2Et·CH(OH)·OEt$, may be separated from the mixture of reduction products by fractional distillation, and forms a colourless liquid, b. p. 136—138°. When heated, it gives rise to an extremely strong odour, and, when mixed with the theoretical amount of phosphoric oxide, decanted, and distilled, it yields ethyl glyoxalate, b. p. 130°, which readily polymerises. When warmed with barium hydroxide, the alcoholate and also glyoxylic acid yield gaseous hydrogen. The alcoholate condenses with ethyl malonate in the presence of acetic anhydride, yielding Perkin and Bishop's ethyl ethylenetricarboxylate (*Proc.*, 1891, **7**, 41), which is hydrolysed with 25% hydrochloric acid to fumaric and malic acids. The ethyl ethylenetricarboxylate reacts with ethyl malonate and sodium ethoxide, forming ethyl propanepentacarboxylate, from which tricarballylic acid is produced on hydrolysis.

Attention is drawn to the fact that many of the products formed by the reduction of ethyl oxalate occur in plant structures (compare Koenigs, *Ber.*, 1892, **25**, 800). J. J. S.

Simple Ester Anhydrides of Saturated Dibasic Organic Acids. D. Mol (*Rec. trav. chim.*, 1907, **26**, 373—408. Compare Abstr., 1906, i, 4).—The ester anhydrides of the dibasic acids are obtained by (1) the action of the monoalkyl chloride on the mixed alkali alkyl salt; (2) the interaction of phosphoryl chloride and a slight excess of the alkali alkyl salt (compare Gerhardt, *Annalen*, 1853, **87**, 237; Geuther, *ibid.*, 1862, **123**, 113), or (3) the action of acetyl chloride on the alkali alkyl salt (compare Bouveault, Abstr., 1900, i, 474).

Ethyl anhydro-oxalate, $O(CO·CO_2Et)_2$, can be prepared by either of the three methods. It is a colourless liquid with a faint odour, b. p. 139°/15 mm., 140°/16 mm., which in a freezing mixture solidifies to crystals, m. p. 8°. The liquid has $D_4^{13·5}$ 1·2480, n_D^{20} 1·42762, n_D^{25} 1·42592. Its ethereal solution reacts with dry ammonia gas, forming ethyl oxamate and ammonium ethyl oxalate. When very rapidly heated at 240°, ethyl anhydro-oxalate decomposes, evolving carbon dioxide, and forming anhydrous ethyl mesoxalate and a liquid having the same empirical formula as the latter, but double its molecular weight. At 150°, the ester anhydride forms carbon monoxide and dioxide, and ethyl formate. Attempts to prepare ethyl anhydromalonate by the second and third methods give no definite result, probably owing to the reactivity of the hydrogen atoms of the $\colon CH_2$ group. The action of potassium ethyl malonate on ethyl malonic chloride has not been studied.

Ethyl anhydrosuccinate, $O(CO·CH_2·CH_2·CO_2Et)_2$, is prepared either by the interaction of sodium ethyl succinate (Blaise, Abstr., 1899, i,

793) and ethyl succinic chloride, obtained by a modification of Michaelis and Hermens' method (Abstr., 1892, 1494), or by the action of phosphoryl chloride on the former salt. It forms colourless crystals, m. p. 28°. In ethereal solution, it is attacked by dry ammonia, forming *ethyl succinamate*, $C_6H_{11}O_3N$, as colourless needles, m. p. 75°, and an extremely deliquescent solid, identified from its reactions as *ammonium ethyl succinate*. When boiled under the ordinary pressure, ethyl anhydrosuccinate carbonises, and after four distillations a mixture of much succinic anhydride and a little ethyl succinate is obtained.

By the action of phosphoryl chloride on sodium ethyl glutarate (obtained by Blaise's method), *ethylanhydroglutarate*, $O(CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, is formed as a colourless liquid, which, when strongly cooled, solidifies to crystals, m. p. 7—8°. The liquid has b. p. 150°/15 mm., $D_4^{13\cdot5}$ 1·1245, n_D^{20} 1·44466, and n_D^{25} 1·44275.

The author points out that the customary method of preparing acid chlorides by addition of phosphoryl chloride to the salt of the acid is contrary to the original directions of Gerhardt, who added the powdered salt to the oxychloride. This would account for the poor yields obtained by some workers.

A vacuum distillation apparatus, based on Dewar's absorption of gases by charcoal cooled in liquid air, is described. E. H.

Synthesis of Methylethylmalic Acid. M. L. SHDANOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, *Chem.*, 1411—1414).—Ethyl α-bromobutyrate reacts with pyruvic acid in the presence of zinc, forming ethyl methylethylmalate, $CO_2Et{\cdot}CHEt{\cdot}CMe(OH){\cdot}CO_2Et$, the yield being 81—84% of the theoretical; when hydrolysed, crystals are formed which could not be purified.

The ammonium salt has m. p. 172·5—174°; at 179°, it resolidifies and then melts at 180—181° (Michael: m. p. 179°); the silver salt has also been obtained. Z. K.

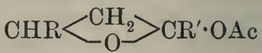
Conversion of Methyl Alcohol into Formaldehyde and the Preparation of Formalin. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1414—1439. Compare Abstr., 1907, i, 892, 1008).—The conversion of methyl alcohol into formaldehyde is not a reversible reaction, and is accompanied by secondary reactions, such as $CH_2O \rightarrow CO + H_2$ and $2H_2 + O_2 = 2H_2O$, &c. The yield of formaldehyde is a maximum when the following relations are observed. The quantity of oxygen : the total quantity of alcohol vapour = 0·4 : 1; oxygen : total quantity of the gaseous mixture = 0·1375 : 1; total quantity of alcohol vapour : total quantity of gaseous mixture = 0·342 : 1. When, in these circumstances, the action proceeds without the application of external energy, $C^2C_1/V^2 = 0{\cdot}00103$ (where C and C_1 = concentration of the methyl alcohol and oxygen respectively, and V = the mean velocity of the gaseous mixture through the catalyst).

The function of the catalyst is discussed at length, the above relations being true when the catalyst consists of a roll of copper gauze 12 cm. in length, 16 mm. transverse section, in which there are 15 × 15 threads in each cubic centimetre.

The ordinary thermodynamic equation for the energy of a reaction is not applicable here. An equation is deduced by which it is possible to calculate the total quantity of gas which should be obtained in any experiment, but it was observed that the quantity actually obtained was always more than that required by this equation, this being due to the absorption of the unknown gas, $(CH_2)_2O$, by the palladium chloride contained in the palladium employed for the absorption of hydrogen. The mixture of gases in the various experiments contains 2% to 18% of this gas, which has an odour resembling slowly oxidising phosphorus and is decomposed at a red-heat. Z. K.

The Ammonia Reaction for Distinguishing between Enolic and Ketonic Derivatives. II. Arthur Michael and Harold Hibbert (*Ber.*, 1907, **40**, 4916—4918. Compare Abstr., 1907, i, 1010).—The untrustworthiness of this reaction is further borne out by the behaviour of enolic ethyl diacetosuccinate in solution. From a light petroleum solution, the ketone is precipitated; from ethyl bromide, the ammonium salt of the enol, and from chloroform a mixture of ketone and enolic salt. Where the enol reacts more readily than the ketone, an almost quantitative separation of the tautomeric substances can be effected with aqueous ammonia. Ketonic dibenzoylacetylmethane and enolic tribenzoylmethane with ammonia in organic solvents both give precipitates. W. R.

Synthesis by Means of Mixed Organo-metallic Compounds of Zinc. Constitution of the β-Acetoxy-ketones. Edmond E. Blaise (*Compt. rend.*, 1907, **145**, 1285—1287).—The β-acetoxyketones, prepared by the condensation of the chlorides of β-acetoxyaliphatic acids with mixed organo-metallic derivatives of zinc (Abstr., 1907, i, 749), do not form crystalline derivatives with either phenylhydrazine, *p*-nitrophenylhydrazine, phenylbenzylhydrazine, or semicarbazide. The only reaction for ketones giving a positive result is obtained with sodium nitro-prusside, which in the presence of a trace of potash produces the characteristic yellowish-red coloration, stable in acetic acid. In order to decide between the alternative formulæ

I. $OAc\cdot CHR\cdot CH_2\cdot COR'$ and II. 

$$CHR<^{CH_2}_{O}>CR'\cdot OAc$$

for the β-acetoxy-ketones, the author has determined their molecular volumes and those of compounds in which a closed lactonic or oxide-chain is known to exist. Whilst in the latter case there are considerable differences between the calculated and observed values due to the closure of the chain, in the former only the normal differences characteristic of open-chain compounds are found. The conclusion is drawn that the β-acetoxy-ketones have the ketonic constitution (I). E. H.

Behaviour of Cellulose with Sodium Hydroxide. O. Miller (*Ber.*, 1907, **40**, 4903—4905. Compare Vieweg, Abstr., 1907, i, 893). —Gladstone's formula for mercerised cellulose, $C_{12}H_{20}O_{10},NaOH$, is not substantiated by the experiments of the author, who finds that the percentage of sodium hydroxide in mercerised cotton increases with the concentration of the alkaline solution. C. S.

Stereochemistry of Chromium. III. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1907, **56**, 261—278).—The paper contains a summary of the mutual relationships of the stereoisomeric chromium salts, and the methods for determining their constitution. Part of the experimental material has already been published (Abstr., 1905, i, 33; 1906, i, 71, ii, 614; 1907, i, 895), and the remainder will be published in detail later (compare next abstract). The more important methods used in determining the constitution of the compounds have already been dealt with (*loc. cit.*). G. S.

Stereochemistry of Chromium. IV. The Isomeric Dibromo-salts. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1907, **56**, 279—295. Compare previous abstract).—It has been shown in earlier papers that the diacidodiethylenediaminechromium salts, $[\mathrm{En_2CrX_2}]\mathrm{X}$ (where En = ethylenediamine, and X = acid group), exist in two stereoisomeric modifications, distinguished as the *cis*-form, $\left[\begin{matrix}\mathrm{En}\\ \mathrm{En}\end{matrix}\!>\!\mathrm{Cr}\!<\!\begin{matrix}\mathrm{X}\\ \mathrm{X}\end{matrix}\right]\mathrm{X}$ (violet salts), and the *trans*-form, $\left[\begin{matrix}\mathrm{En}\\ \mathrm{X}\end{matrix}\!>\!\mathrm{Cr}\!<\!\begin{matrix}\mathrm{En}\\ \mathrm{X}\end{matrix}\right]\mathrm{X}$ (green salts), respectively. In the present paper, the dibromo-salts and certain of their derivatives are described. Their constitution has been established mainly from their relationship to the dioxalato-salts already described.

cis-*Dibromodiethylenediaminechromium bromide*, $[\mathrm{En_2CrBr_2}]\mathrm{Br,H_2O}$, and the corresponding *iodide* and *dithionate*, described in a previous paper (Abstr., 1907, i, 895), have been more fully investigated.

trans-*Dibromodiethylenediaminechromium bromide*, $[\mathrm{En_2CrBr_2}]\mathrm{Br,H_2O}$ (microscopic, green plates), is prepared by evaporating an aqueous solution of the diaquo-salt, $[\mathrm{En_2Cr(O_2H_4)Br}]\mathrm{Br_2}$, with hydrobromic acid in the presence of mercuric bromide. A double salt, $[\mathrm{En_2CrBr_2}]\mathrm{Br,HgBr_2}$, separates as a green, lustrous, crystalline powder; on the removal of the mercury by means of hydrogen sulphide, a green solution containing the *trans*-salt is obtained.

The corresponding salts described below are obtained from the green solution by double decomposition with the alkali salt of the corresponding acid. All, including the bromide itself, are soluble in water, but the solutions are very unstable, the intraradicle bromine is eliminated, and the colour changes simultaneously from green to yellowish-brown.

With concentrated hydrobromic acid, the compound, $[\mathrm{En_2CrBr_2}]\mathrm{Br}$, gives a double salt, $[\mathrm{En_2CrBr_2}]\mathrm{Br,HBr,2H_2O}$, which occurs in grass-green, transparent plates, and is very unstable.

trans-*Dibromodiethylenediaminechromium dithionate*, $[\mathrm{En_2CrBr_2}]\mathrm{S_2O_6}$, occurs in lustrous, flat, green needles; the corresponding *iodide*, *nitrate*, and *thiocyanate* also form lustrous, green needles.

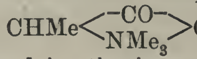
The *compound*, $[\mathrm{En_2CrI_2}]\mathrm{I,HgI_2}$, obtained by the action of hydriodic acid on a solution of the bromobisaquobromide and mercuric iodide, occurs in lustrous, deep green leaflets, almost insoluble in water.

trans-*Dichlorodiethylenediaminechromium dithionate*, $[\mathrm{En_2CrCl_2}]\mathrm{S_2O_6}$, prepared by the general method, occurs in lustrous, red needles, which turn green on rubbing.

trans-*Dichlorodiethylenediaminechromium platinichloride*,

$$[\mathrm{En_2CrCl_2}]\mathrm{PtCl_6,12H_2O},$$

obtained by the action of chloroplatinic acid on the corresponding chloride, forms small, yellowish-green needles. G. S.

Optically Active Trimethyl-α-propiobetaine (α-Homobetaine). Emil Fischer (*Ber.*, 1907, 40, 5000—5008. Compare Abstr., 1907, i, 192).—l-*Trimethylpropiobetaine*,  $\mathrm{CHMe}{<}\genfrac{}{}{0pt}{}{-\mathrm{CO}-}{\mathrm{NMe_3}}{>}\mathrm{O}$ (compare Brühl, this Journ., 1876, i, 698), prepared by the interaction of *d*-bromopropionic acid with trimethylamine in the cold, forms colourless plates, decomp. 242° (corr.), $[\alpha]_D^{20}$ $-19{\cdot}7°$. It forms two dimorphous aurichlorides (compare the behaviour of betaine, Fischer, Abstr., 1902, i, 428, and Willstätter, *loc. cit.*, 266), the one crystallising in lustrous, gold-coloured, thin crystals, m. p. 259° (decomp., corr.), from the acid solution, and the other forming a yellow powder consisting of microscopic, short needles, aggregated in crosses or six-armed stars, m. p. 226° (corr.), obtained on crystallisation from warm water. They give the unchanged active betaine when decomposed with hydrogen sulphide. An identical trimethylpropiobetaine is obtained by the action of methyl iodide on *d*-alanine. The action of ammonia and of trimethylamine on *d*-α-bromopropionic acid takes place accordingly in the same stereochemical sense, whilst it has already been shown that no Walden rearrangement takes place in the case of ammonia.

By the interaction of trimethylamine and ethyl *d*-α-bromopropionate in alcoholic solution at the room temperature, the *compound*,

$$CH_3{\cdot}CH(NMe_3Br){\cdot}CO_2Et,$$

is formed quantitatively in large, colourless needles, m. p. 150—151° (corr.), but is quite optically inactive, and is identical with that formed from inactive ethyl α-bromopropionate. The *aurichloride* separates in very thin, characteristic, yellow plates, m. p. 96—97° (corr.). The compound yields inactive trimethyl α-propiobetaine when treated with silver oxide. It is possible by interrupting the reaction at an early stage to obtain a product having $[\alpha]_D$ $-8{\cdot}1°$, which yields a propiobetaine, $[\alpha]_D$ $-3{\cdot}2°$, that is about five-sixths racemised. Excess of trimethylamine rapidly racemises salts of ethyl trimethylaminopropionate, but is without action on salts of ethyl *d*-alanine ester. It would appear that the mere presence of a quaternary ammonium group is sufficient greatly to increase the tendency of the betaine to racemise, autoracemisation at a low temperature being characteristic of optically active quinquevalent nitrogen derivatives. E. F. A.

Oxidation of Leucine, α-Amino*iso*valeric Acid, and α-Amino-*n*-valeric Acid with Hydrogen Peroxide. Henry D. Dakin (*J. Biol. Chem.*, 1908, 4, 63—76).—Leucine on oxidation with hydrogen peroxide yields *iso*valeraldehyde, *iso*valeric acid, ammonia, and carbon dioxide. On further oxidation, acetone is formed from the *iso*valeric acid. The reaction closely resembles several biochemical changes in which leucine takes part. Breinl and Baudisch's statement as to the formation of *iso*butaldehyde is incorrect, and the product Liebig described when lead peroxide is used is not butaldehyde, but *iso*valeraldehyde. α-Amino*iso*valeric acid, under similar conditions, yields *iso*butaldehyde, *iso*butyric acid, ammonia, and carbon dioxide.

Part of the *iso*butyric acid is further oxidised with acetone and carbon dioxide. With lead peroxide, α-amino*iso*valeric acid yields *iso*butaldehyde.

α-Amino-*n*-valeric acid on oxidation yields *n*-butaldehyde, butyric acid, ammonia, and carbon dioxide. On further oxidation, the butyric acid is, in part, decomposed with formation of acetone, aldehydes, lower fatty acids, and carbon dioxide.

The first steps in the oxidation of each of the above amino-acids are analogous to those observed in other amino-acids, and may be expressed as follows:

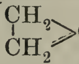
$$R\cdot CH(NH_2)\cdot CO_2H + O = R\cdot CHO + NH_3 + CO_2.$$
$$R\cdot CH(NH_2)\cdot CO_2H + O_2 = R\cdot CO_2H + NH_3 + CO_2.$$

W. D. H.

Action of Nitrous Acid on Allylamine. Louis Henry (*Compt. rend.*, 1907, **145**, 1247—1249).—When an aqueous solution of allylamine neutralised by hydrochloric acid is treated with sodium nitrite, allyl alcohol is the sole product. This shows that at the moment of formation the allyl alcohol does not undergo the isomeric change:

$$CH_2{:}CH\cdot CH_2\cdot OH \longrightarrow CH_2{:}C(OH)\cdot CH_3,$$

which occurs in the saturated propyl alcohol, since the unsaturated alcohol, $CH_2{:}C(OH)\cdot CH_3$, would be immediately transformed into acetone, and this is not formed. Thus allylamine behaves differently from propylamine towards nitrous acid. The action of nitrous acid on allylamine may be compared with that on trimethyleneamine, which gives, not *iso*allyl alcohol,



$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!CH\cdot OH$, but allyl alcohol (Kijner, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 377).

The action of sodium nitrite on dibromopropylamine hydrochloride, $CH_2\cdot Br\cdot CHBr\cdot CH_2NH_2,HCl$ (Henry, *Ann. Soc. Sci. Brussels*, 1880, **4**, 317), appears to be more complicated than the reaction with allylamine.

E. H.

Preparation of Methyl and Ethyl Cyanides. Victor Auger (*Compt. rend.*, 1907, **145**, 1287—1290).—Potassium cyanide in concentrated aqueous solution acts on (1) methyl sulphate, giving 92% of the theoretical yield of acetonitrile; (2) ethyl sulphate, 90% of propionitrile; (3) sodium methyl sulphate (which, contrary to Beilstein, is not anhydrous, but contains $1H_2O$), 92% of acetonitrile and 0·2—0·8% of methylcarbylamine; (4) potassium ethyl sulphate, 75% propionitrile and 0·45% of ethylcarbylamine (using the dry salts only, 55% of propionitrile is obtained); (5) methyl iodide, 95% acetonitrile, and (6) ethyl iodide in the presence of methyl alcohol, 97% of propionitrile in the form of its constant boiling mixture with methyl alcohol.

In the last two cases, the carbylamine if formed would be destroyed by the alkyl iodide. Thus, whilst Guillemard's results (Abstr., 1907, i, 300) lead to the conclusion that potassium cyanide has the *iso*cyanide constitution when in the solid state, those of the author assign to it a normal structure when in aqueous solution.

E. H.

Preparation of *cyclo*Propane. GABRIEL GUSTAVSON (*J. pr. Chem.*, 1907, [ii], 76, 512. Compare Willstätter and Bruce, Abstr., 1907, i, 1018).—In the author's method of preparing *cyclo*propane (Abstr., 1888, 240; 1899, i, 421) by the action of zinc dust on trimethylene dibromide, the reaction is carried out in 75% alcohol, and the temperature is raised above 60° only towards the end. The first portions of the product are rejected, as the trimethylene dibromide always contains propylene dibromide. G. Y.

Synthesis of *o*-Nitrotriphenylmethane. ALFRED KLIEGL (*Ber.*, 1907, 40, 4937—4942. Compare Baeyer and Löhr, Abstr., 1900, 1141).—*o*-Nitrotriphenylmethane cannot be obtained by condensing *o*-nitrobenzaldehyde with benzene. The product is a colourless resin, which is completely soluble in concentrated sulphuric acid. The desired compound may be prepared readily from *o*-nitrobenzylidene chloride and benzene by Friedel and Crafts' synthesis.

o-Nitrobenzylidene chloride, $NO_2\cdot C_6H_4\cdot CHCl_2$ (70—75%), and a small amount of *a-a-dichloro-2 : 2′-dinitrobenzyl ether*,

$$(NO_2\cdot C_6H_4\cdot CHCl)_2O$$

(5%), are formed by the action of phosphorus pentachloride on a benzene solution of *o*-nitrobenzaldehyde. The benzylidene chloride is a lemon-yellow liquid, b. p. 143—144°/12 mm., and solidifies in a freezing mixture. It decomposes on exposure to light, or when kept for some time in contact with the atmosphere. When warmed with concentrated sulphuric acid, the aldehyde (40%) is regenerated. The benzyl ether is probably identical with the product obtained by Zimmermann and Müller (Abstr., 1885, 771). A better yield (29%) is obtained by the action of phosphorus pentachloride on a well-cooled chloroform solution of the aldehyde. It is very sparingly soluble in all the ordinary solvents, but may be crystallised from pure ethyl acetate, and decomposes at about 180°. When boiled with acetic acid, it yields the aldehyde, and with alcohol the *diethylacetal* of the aldehyde, $NO_2\cdot C_6H_4\cdot CH(OEt)_2$, b. p. 154—156°/18 mm.

o-*Nitrotriphenylmethane*, $C_{19}H_{15}O_2N$, is best obtained when the reaction mixture, with an excess of benzene, is kept at the ordinary temperature for several days, and then decomposed with dilute hydrochloric acid. It crystallises from alcohol in pale yellow, glistening plates, or from light petroleum (100—140°) in compact prisms, m. p. 93—94°, and does not give a coloration with alcoholic potassium hydroxide. J. J. S.

Action of Dichloroacetic Acid on Aniline and its Homologues. I. IWAN VON OSTROMISSLENSKY (*Ber.*, 1907, 40, 4972—4979).—When *o*-toluidine is treated with dichloroacetic acid, the author was unable to detect the formation of di-*o*-toluidinoacetic acid according to Meyer (Abstr., 1884, 47); the main product of the action was o-*methylaminophenyl*-o-*toluidinoacetic acid*, $C_{16}H_{18}O_2N_2$, which separates from alcohol in prismatic needles, m. p. 239—240° (decomp.). o-*Tolyl*-o-*methylimesatin*, $C_{16}H_{14}ON_2$, obtained as a by-product, separates from alcohol in glistening, golden-yellow leaflets, m. p. about 225° (decomp.); when boiled with acids, it forms *o*-methylisatin and the toluidine salt.

The mechanism of the interaction of *o*-toluidine and dichloroacetic acid is discussed, and the results obtained by Meyer from the action of *p*-toluidine on dichloroacetic acid are confirmed.

The action of aniline on dichloroacetic acid was also studied.

A. McK.

Salts and Ethers of Hexanitrodiphenylamine. D. K. Alexandroff (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, *Chem.*, 1391—1395).—*s*-Hexanitrodiphenylamine, $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_2(NO_2)_3$, is a typical example of a pseudo-acid (compare Hantzsch, Abstr., 1906, i, 576, 651, 833, 856); thus, whilst it is itself a slightly-coloured non-electrolyte, its salts, which are either the *syn*- or *anti*-derivatives, are all brightly coloured. The sodium, lithium, silver, and ammonium salts are red; the potassium and rubidium salts dark violet; they all correspond with the formula $C_{12}H_4O_{12}N_7M$. The crystalline forms of the two series are different, but they all form bright yellow solutions. From the silver salt, red solutions of either the *syn*- or *anti*-methyl and propyl ethers were formed, which could not be isolated. Z. K.

Which Substances Contain a Readily Resolvable Single Carbon–Nitrogen Linking? Hermann Emde (*J. pr. Chem.*, 1907, [ii], **76**, 509—511. Compare Mohr, Abstr., 1907, i, 721).—It was shown previously that, on reduction with sodium amalgam, cinnamyltrimethylammonium chloride, $CHPh{:}CH \cdot CH_2 \cdot NMe_3Cl$, yields trimethylamine hydrochloride and α-phenylpropylene (Schmidt and Emde, Abstr., 1906, i, 945). On the other hand, the corresponding chlorohydrin, formed by addition of hypochlorous acid to the ethylene linking, when reduced with sodium amalgam yields an amino-alcohol, hydrogen being substituted for the chlorine atom. Hence the C–N linking in the cinnamylamine is rendered unstable by the ethylene linking in the grouping $C{:}C \cdot C \cdot N$. G. Y.

Action of the Chlorides of Phosphorus on Phenolsulphonic Acids. I. Richard Anschütz (*Annalen*, 1907, **358**, 92—97).—The action of phosphorus pentachloride on phenol-*p*-sulphonic acid, if analogous to that of the pentachloride on *p*-hydroxybenzoic acid (Abstr., 1906, i, 500), must lead to the formation in the first place of phosphoryl chloride and phenol-*p*-sulphonyl chloride, and thereafter to that of chlorosulphophenyl dichloro-orthophosphate,

$$SO_2Cl \cdot C_6H_4 \cdot O \cdot POCl_2,$$

whereas Kekulé obtained *p*-chlorophenylphosphoryl chloride (this Journ., 1873, 1239). On re-investigation of the reaction, it has been found that Kekulé's compound is formed only if the immediate product is distilled under the ordinary pressure. The *dichlorophosphate*,

$$C_6H_4O_4Cl_3SP,$$

is obtained if the product of the action of phosphorus pentachloride on potassium phenol-*p*-sulphonate is extracted with light petroleum; it crystallises in colourless needles, m. p. 87—88°, b. p. 203°/13·5 mm.

2 : 6-*Dibromo-4-chlorosulphophenyl dichlorophosphate*,

$$SO_2Cl \cdot C_6H_2Br_2 \cdot O \cdot POCl_2,$$

prepared in the same manner from potassium 2:6-dibromophenol-4-sulphonate, separates from carbon tetrachloride as a hygroscopic, white, crystalline crust, m. p. 76—78° (compare Zincke and Glahn, Abstr., 1907, i, 698). G. Y.

Oxidation of Thymol by the Oxidising Ferment of Mushrooms. H. Cousin and Henri Hérissey (*J. Pharm. Chim.*, 1907, [vi], 26, 487—491. Compare Bougault, Abstr., 1902, i, 638).—When an aqueous solution of thymol is treated with the oxidising ferment of mushrooms in the presence of air, a white precipitate is formed (Bourquelot, Abstr., 1897, ii, 66). The authors have prepared this precipitate by means of the ferment obtained from *Russula delica* and from *Lactarius controversus*. It contains the dithymol, $C_{20}H_{26}O_2,H_2O$, m. p. 100—101°, described by Dianine (Abstr., 1882, 623), which, after the first melting, resolidifies, and again melts at 164·5° (corr.) (Dianine gives 165·5°), the m. p. of the anhydrous substance. The dithymol so formed is very pure, giving colourless solutions in alkalis instead of the orange solutions obtained by Dianine. The ferment obtained from the second source gives a less pure product. The white precipitate contains other compounds which seem to be of a quinonoid nature, and have not yet been obtained crystalline. The oxidation product of thymol has no antiseptic power, and the authors conclude that in many circumstances thymol is a bad antiseptic agent. E. H.

Sulphoxides and Sulphines. Karl A. Hofmann and K. Ott (*Ber.*, 1907, 40, 4930—4936).—A solution of ferric chloride in thionyl chloride reacts with heptane from petroleum, yielding a blood-red oil, which gradually solidifies to a black, crystalline mass of *ditolylsulphoxide ferrichloride*, $SO(C_7H_7)_2,FeCl_3$, m. p. 60·5°. It decomposes when heated with water, yielding ditolylsulphoxide and ferric chloride, and dissolves readily in chloroform to an intense reddish-violet solution, which shows two absorption bands, 660—680 $\mu\mu$ and 520—618 $\mu\mu$, in addition to complete absorption from 440 $\mu\mu$ in the violet end. Toluene yields the same product.

A molecular mixture of benzyl sulphide and benzyl chloride reacts with an ethereal solution of ferric chloride, yielding *tribenzylsulphine chloride ferrichloride*, $S(C_7H_7)_3Cl,FeCl_3$, which crystallises from alcohol in pale yellowish-green, twinned plates, m. p. 98·5°. *Bistribenzylsulphine chloride ferrichloride*, $2S(C_7H_7)_2Cl,FeCl_3$, is formed when excess of benzyl chloride is used, or by the action of thionyl chloride and benzyl chloride on ferric chloride at the ordinary temperature. It forms thick, glistening, crystalline plates, m. p. 97—107° (decomp.). *Tribenzylsulphine platinichloride*, $[S(C_7H_7)_3]_2PtCl_6$, is insoluble in water, and has m. p. 186°. *Tribenzylsulphine iodide* forms a pale yellow powder, m. p. 75°, and the *ferrocyanide*, $S(C_7H_7)_3H_3FeC_6N_6$, a white precipitate which decomposes at 180°.

Benzyl chloride and benzyl sulphide do not appear to react in the absence of ferric chloride. The following mixed sulphine chlorides have been prepared with the aid of ferric chloride, and from the ferrichlorides the ferrocyanides have been obtained by precipitating with ammonia and adding potassium ferrocyanide solution to the filtrate: dibenzyl-*tert.*-butylsulphine chloride, diethyl-*tert.*-butylsulphine chloride, benzyldiethylsulphine chloride, dibenzyl ethylsulphine chloride, and triethylsulphine chloride.

The ferrocyanides form white precipitates, all of which, with the exception of the last, are insoluble in water.

The accelerating effect of the ferric chloride appears to be due to the formation of an additive compound of the chloride with the sulphide, $\substack{R\\R}>S<\substack{FeCl_2\\Cl}$. J. J. S.

Transformation of the Tetramethylene Ring into the Trimethylene Ring. NICOLAUS J. DEMJANOFF (*Ber.*, 1907, **40**, 4961—4963).—Perkin (Trans., 1894, **65**, 950) found that when *cyclo*butylamine, $NH_2\cdot CH<\substack{CH_2\\CH_2}>CH_2$, is acted on by nitrous acid, an alcohol, C_4H_8O, is formed, to which he assigned the formula $OH\cdot CH<\substack{CH_2\\CH_2}>CH_2$. The author concludes that, in the action in question, the tetramethylene ring is converted into the trimethylene ring.

The alcohol, C_4H_8O, has b. p. 123—124°. It was oxidised by means of a mixture of chromic and sulphuric acids in aqueous solution; the oxidation product exhibited reactions typical of aldehydes, and the semicarbazone prepared from it was by no means uniform, since by treatment with ether it was resolved into *cyclo*butanonesemicarbazone, m. p. 202°, and a semicarbazone, m. p. 126—127°, which has all the properties of *cyclo*propaldehydesemicarbazone. The latter compound is decomposed by dilute acids to form an aldehyde.

It is concluded that the oxidation product of the alcohol, obtained from the amine, $NH_2\cdot CH<\substack{CH_2\\CH_2}>CH_2$, is a mixture of *cyclo*butanone and *cyclo*propanealdehyde. A. McK.

***cyclo*Butylcarbinol and its Isomerisation to Pentamethylene Derivatives.** NICOLAUS J. DEMJANOFF (*Ber.*, 1907, **40**, 4959—4961).—*cyclo*Butylcarbinol, $OH\cdot CH_2\cdot CH<\substack{CH_2\\CH_2}>CH_2$ (compare Perkin, Trans., 1901, **79**, 329), may be conveniently prepared by the reduction of ethyl *cyclo*butanecarboxylate by means of sodium and alcohol according to Bouveault and Blanc's method. It is a transparent, thick oil, b. p. 142—142·5°/750 mm., D_{10}^{10} 0·9199, D_{20}^{20} 0·9129, n_D^{19} 1·4449. When warmed with concentrated hydrobromic acid, it is converted into the *bromide*, C_5H_9Br, a transparent liquid, b. p. 137—139°, D_{19}^{19} 1·400, n_D^{19} 1·4875. When reduced, a hydrocarbon, C_5H_{10}, is formed with b. p. 49·5—50°; the properties of this hydrocarbon agree with those of *cyclo*pentane, but differ from those of methyl*cyclo*butane.

A. McK.

Aromatic Alcohols. New Reactions. ROBERT FOSSE (*Compt. rend.*, 1907, **145**, 1290—1293).—Benzhydrol-*p*-dimethylamine similarly to xanthhydrol and dinaphthapyranol (Abstr., 1906, i, 975 and benzhydrol-*p-p*-tetramethyldiamine (Abstr., 1907, i, 414), condenses with methylenic derivatives with elimination of water, thus:

$$NMe_2\cdot C_6H_4\cdot CHPh\cdot OH + H\cdot CHXY = H_2O + NMe_2\cdot C_6H_4\cdot CHPh\cdot CHXY.$$

By this reaction, p-*dimethylaminobenzhydrylbenzoylacetone*,

$$NMe_2\cdot C_6H_4\cdot CHPh\cdot CH(COPh)\cdot COMe,$$

small, faintly sulphur-yellow crystals, m. p. 157—158°, and p-*dimethylaminobenzhydrylacetylacetone*, colourless needles, m. p. 131°, are obtained. In the same way, benzhydrol itself reacts with β-ketonic esters and β-diketones, giving compounds hitherto only obtainable by the action of a halogen derivative of diphenylmethane on the sodium compound of the methylenic derivative. By this new reaction, there were prepared: *ethyl benzhydrylbenzoylacetate*,

$$CHPh_2\cdot CH(COPh)\cdot CO_2Et,$$

needles, m. p. 135° (on mercury); *benzhydrylbenzoylacetone*,

$$CHPh_2\cdot CH(COPh)\cdot COMe,$$

fine, white needles, m. p. 148—150°, and *benzhydrylacetylacetone*,

$$CHPh_2\cdot CH(COMe)_2,$$

m. p. 116° (on mercury).

The hydroxyl of different diaryl secondary alcohols will also combine with methylenic hydrogen, forming the compounds: *ethyl phenyl-α-naphthylmethylbenzoylacetate*, ${}^{\alpha}C_{10}H_7\cdot CHPh\cdot CH(COPh)\cdot CO_2Et$, m. p. 160° (varies with duration of heating); *phenyl-α-naphthylmethylacetylacetone*, ${}^{\alpha}C_{10}H_7\cdot CHPh\cdot CH(COMe)_2$, m. p. 126° (on mercury); *phenyl-α-naphthylmethylbenzoylacetone*,

$${}^{\alpha}C_{10}H_7\cdot CHPh\cdot CH(COPh)\cdot COMe,$$

m. p. 185—185·5°; p-*methylbenzhydrylacetylacetone*,

$$CH_3\cdot C_6H_4\cdot CHPh\cdot CH(COMe)_2,$$

m. p. 104—106°, and p-*methylbenzhydrylbenzoylacetone*,

$$CH_3\cdot C_6H_4\cdot CHPh\cdot CH(COPh)\cdot COMe,$$

m. p. 130° (on mercury).

By the action of methyl malonate on triphenylcarbinol, carbon dioxide, methyl alcohol, methyl acetate, and *methyl triphenylmethylmalonate*, m. p. 130—131° (on mercury), are formed, thus:

$$CPh_3\cdot OH + 2CH_2(CO_2Me)_2 = CO_2 + MeOH + CH_3\cdot CO_2Me + CPh_3\cdot CH(CO_2Me)_2.$$

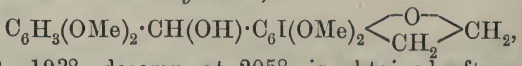
This reaction with ethyl malonate gives Henderson's ethyl triphenylmethylmalonate and, at the same time, triphenylmethane according to the equation:

$$CPh_3\cdot OH + CH_2(CO_2Et)_2 = CO_2 + CH_3\cdot CHO + CH_3\cdot CO_2Et + CHPh_3.$$

Hitherto, it has been possible to replace the oxygen in aldehydes by the group $:CXY$, but not the hydroxyl in alcohols by the group $\cdot CHXY$.

E. H.

Catechin. Stanislaus von Kostanecki and Victor Lampe (*Ber.*, 1907, **40**, 4910—4912. Compare Abstr., 1902, i, 553, 637; 1907, i, 73).—*Iodocatechin tetramethyl ether*,

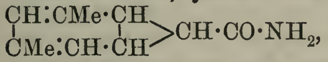
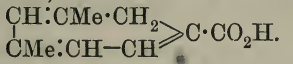


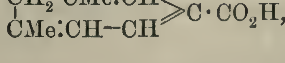
$$C_6H_3(OMe)_2\cdot CH(OH)\cdot C_6I(OMe)_2 < \substack{-O-\\ CH_2} > CH_2,$$

m. p. 192—193°, decomp. at 205°, is obtained after a few hours when alcoholic solutions of catechin tetramethyl ether and of iodine and iodic acid are mixed; it separates from alcohol in long, white needles, forms an *acetate*, $C_{21}H_{23}O_7I$, m. p. 189°, and develops a yellow colour with concentrated sulphuric acid, which after a time becomes violet. The halogen is readily eliminated by zinc dust and alkali, catechin tetramethyl ether being regenerated.

Other halogenated phloroglucinol derivatives in alcoholic solution lose the halogen in a similar manner. Ciamician and Silber's bromomaclurin pentamethyl ether (bromoveratroylphloroglucinol trimethyl ether) is converted into leucomaclurin pentamethyl ether (2 : 4 : 6 : 3′ - 4′-pentamethoxybenzhydrol), whilst phloroglucinol trimethyl ether is regenerated from *dibromophloroglucinol trimethyl ether*, $C_6HBr_2(OMe)_3$, m. p. 132—133°, which is obtained by the bromination of the trimethyl ether in glacial acetic acid. C. S.

Ethyl Diazoacetate and *m*-Xylene. Eduard Buchner and Konrad Delbrück (*Annalen*, 1907, **358**, 1—35).—Buchner and his co-workers in a series of investigations (Abstr., 1896, i, 230; 1897, i, 282; 1898, i, 639; 1900, i, 292; 1901, i, 385) have shown that the product of the action of ethyl diazoacetate on benzene is ethyl norcardienecarboxylate, a derivative of a dicyclic system consisting of a three-atom and a six-atom ring, making together a seven-atom ring. Buchner and Feldmann (Abstr., 1904, i, 57) have found the action of ethyl diazoacetate on toluene to lead to the formation of ethyl 3-methylnorcardiene-7-carboxylate or of the products of the conversion of this into derivatives of the methylated seven-atom ring. In the present paper, the substances obtained from ethyl diazoacetate and *m*-xylene are described and their constitutions discussed.

The almost colourless *oil*, b. p. 129°/10 mm., obtained on fractionally distilling the product of the action of ethyl diazoacetate on *m*-xylene, yields analytical figures corresponding with ethyl dimethylnorcardienecarboxylate, but is a mixture containing comparatively little of this ester. The *oil*, b. p. 115—125°/10 mm., obtained in the same manner from methyl diazoacetate, when shaken with aqueous ammonia at 0°, yields 3 : 5-*dimethyl*-$\Delta^{2,4}$-*norcardiene*-7-*carboxylamide*,  $\begin{matrix}\mathrm{CH{:}CMe{\cdot}CH}\\ \mathrm{CMe{:}CH{\cdot}CH}\end{matrix}\!>\!\mathrm{CH{\cdot}CO{\cdot}NH_2}$, which crystallises in colourless needles, m. p. 142°, and reduces permanganate in sodium carbonate solution. When boiled with 30% sulphuric acid, the amide is hydrolysed, forming 1 : 3-dimethylphenyl-4-acetic acid, but, if boiled with 5% sodium hydroxide, it forms 3 : 5-*dimethyl*cyclo-$\Delta^{3,5,7}$-*heptatriene*-1-*carboxylic acid*,  $\begin{matrix}\mathrm{CH{:}CMe{\cdot}CH_2}\\ \mathrm{CMe{:}CH{-}CH}\end{matrix}\!\geqslant\!\mathrm{C{\cdot}CO_2H}$. This crystallises in leaflets, m. p. 151°, decolorises permanganate in sodium carbonate solution, gives with concentrated sulphuric acid a yellow coloration resembling picric acid, and, when boiled with aqueous sodium hydroxide, yields an acid, m. p. 113°.

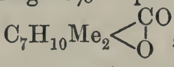
The hydrolysis of the crude ethyl dimethylnorcardienecarboxylate with sodium hydroxide leads to the formation of 3 : 5-*dimethyl*-cyclo-$\Delta^{2,5,7}$-*heptatriene*-1-*carboxylic acid*,  $\begin{matrix}\mathrm{CH_2{\cdot}CMe{:}CH}\\ \mathrm{CMe{:}CH{-}CH}\end{matrix}\!\geqslant\!\mathrm{C{\cdot}CO_2H}$, which crystallises in flat needles, m. p. 148°, decolorises permanganate in sodium carbonate solution, but is stable in air, and gives a yellow coloration with concentrated sulphuric acid. The *magnesium, calcium*, and *barium* salts are readily, but the *salts* of the heavy metals only sparingly, soluble; the *silver* salt, $C_{10}H_{11}O_2Ag$, is hygroscopic, and when heated evolves the free acid, m. p. 148°. The *amide*, $C_{10}H_{13}ON$, crystallises in colourless needles, m. p. 107°, becomes yellow and resinous on exposure to air, reduces permanganate in sodium carbonate solution, gives the characteristic yellow coloration with concentrated sulphuric acid, and, on hydrolysis with alkalis, yields the acid, m. p. 148°. On treatment with bromine in glacial acetic acid solution under cooling, the acid forms a *dibromide*, $C_{10}H_{12}O_2Br_2$, which is obtained as a white, crystalline powder, becomes yellow on exposure to light, or at 100°, decomp. 185°, and is only partly soluble in aqueous sodium carbonate. The action of hydrogen bromide on the acid, m. p. 148°, leads to the formation of 1 : 3-dimethylphenyl-4-acetic acid, m. p. 105°; the *amide*, $C_{10}H_{13}ON$, crystallises in colourless needles, m. p. 183°. In some cases, the formation of an unstable *product*, intermediate between the dimethyl*cyclo*heptatrienecarboxylic acid and the dimethylphenylacetic acid, was observed.

3 : 5-*Dimethyl*cyclo-$\Delta^{1,5}$-*heptadiene*-1-*carboxylic acid*,

$$C_7H_7Me_2{\cdot}CO_2H,$$

prepared by reduction of the heptatrienecarboxylic acid, m. p. 148°, with sodium amalgam in presence of carbon dioxide, crystallises in colourless needles, m. p. 123°, decolorises permanganate in sodium carbonate solution, is readily oxidised by air, and does not give a coloration with concentrated sulphuric acid. The *amide* crystallises in colourless leaflets, m. p. 101°. The *dibromide*, decomp. 175°, decolorises permanganate.

3 : 5-*Dimethyl*cyclo-Δ^5-*heptene*-1-*carboxylic acid*, $C_7H_9Me_2{\cdot}CO_2H$, prepared by reduction of the *cyclo*heptatriene- or *cyclo*heptadienecarboxylic acid with sodium amalgam in boiling sodium carbonate solution in presence of a current of carbon dioxide, separates from dilute alcohol in crystals, m. p. 80°, decolorises permanganate in sodium carbonate and bromine in glacial acetic acid solution, is not further reduced by sodium amalgam, and does not undergo transformation when boiled with aqueous potassium hydroxide. The *amide* crystallises in leaflets, m. p. 167—168°. The acid is converted by the action of hydrogen bromide in glacial acetic acid solution at 100°, or of boiling 50% sulphuric acid, into 3 : 5-*dimethyl*cyclo*heptane*-γ-*carbolactone*,



$C_7H_{10}Me_2{<}\begin{array}{c}\mathrm{CO}\\ |\\ \mathrm{O}\end{array}$, which crystallises from light petroleum in stout prisms, m. p. 76°, and, when boiled with aqueous sodium hydroxide, forms the *sodium* salt of the corresponding hydroxy-acid, which is isolated in the form of its *silver* salt as a white precipitate.

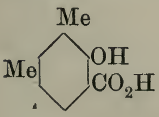
3 : 5-*Dimethyl*cyclo*heptanecarboxylic acid*, $C_{10}H_{18}O_2N$, prepared by reduction of the three preceding unsaturated acids with sodium in amyl alcoholic solution, is obtained as an oil with an odour resembling that of the fatty acids. The *amide*, $C_{10}H_{19}ON$, crystallises in white

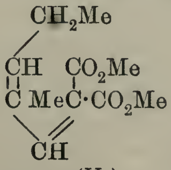
needles, m. p. 157°; the *silver* salt, $C_{10}H_{17}O_2Ag$, forms yellow leaflets.
G. Y.

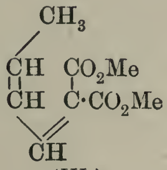
A Case of the Inhibiting Action of the Carboxyl Group. Maximilian Nierenstein and T. A. Webster (*Ber.*, 1908, **41**, 80—81).—The condensation of various phenols and phenolic acids with formaldehyde in the presence of hydrochloric acid to insoluble diphenylmethane derivatives (compare Abstr., 1907, ii, 192) has been studied. With all phenols, the precipitate obtained is completely insoluble in hot water; with hydroxy-acids the amount of precipitate is often less, and only a portion is insoluble in boiling water. The soluble portion consists of hydroxyaurincarboxylic acids. With protocatechuic acid and vanillic acid, precipitates were not obtained.
J. J. S.

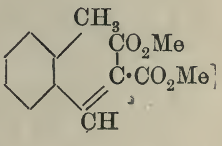
Constitution of Phenylnaphthalenedicarboxylic Acid. A Reply to Stobbe. Arthur Michael and John E. Bucher (*Ber.*, 1908, **41**, 70—73. Compare Stobbe, Abstr., 1907, i, 769).—The formation of *o*-benzoylbenzoic acid by the oxidation of 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride has been already mentioned by the authors. Most of the differences between Stobbe's results and those obtained previously by the authors (Abstr., 1898, i, 256) are due to the fact that Stobbe did not follow the authors' detailed instructions.
J. J. S.

Condensation Reactions of *αβ*-Unsaturated Aldehydes; Formation of Benzene Rings. Hans Meerwein (*Annalen*, 1907, **358**, 71—91).—The formation of aromatic from aliphatic compounds takes place in some cases with great ease, whilst analogously constituted substances may not undergo ring condensation. Thus, whereas the condensation product of methylethylacraldehyde and acetone is readily transformed into *ψ*-cumene (Barbier and Bouveault, Abstr., 1895, i, 643), Dautwitz (Abstr., 1906, i, 803) was unable to obtain *p*-xylene from the condensation product of tiglic aldehyde and acetone. The present author, who has undertaken a systematic investigation of the factors determining the formation or non-formation of rings in such cases, finds that *o*-hydroxymesitylenic acid (I) is formed from the condensation product (II) of methylethylacraldehyde and methyl malonate, but that the condensation products of crotonaldehyde (III) and tolualdehyde (IV) with methylmalonate do not form aromatic hydroxy-acids:


(I.)


(II.)


(III.)


(IV.)

The ring formation is evidently determined by the presence of substituting groups, and by their position. Attempts to prepare aromatic hydrocarbons from the condensation products of crotonaldehyde and *o*-tolualdehyde with acetone were unsuccessful.

Condensation of αβ-Unsaturated Aldehydes with Methyl Malonate: Synthesis of Homologous Salicyclic Acids.—Methyl citralidenemalonate, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}C(CO_2Me)_2$, formed in a 63% yield by the action of citral on methyl malonate in presence of piperidine at − 10°, is obtained as a viscid oil, b. p. 190—195°/20 mm., D^{15} 1·043, n_D^{15} 1·5126; the mol. refraction observed, 76·60, is considerably greater than the calculated, 73·73, as has been found by other authors in the case of compounds containing conjugated ethylene linkings. When boiled with sodium hydroxide in alcoholic solution, the ester is converted into an acid which is either 4-*methyl*-3-iso*amenylsalicylic acid,*

$$CMe_2{:}CH{\cdot}CH_2{\cdot}C_6H_2Me(OH){\cdot}CO_2H,$$

or 4-iso*hexenylsalicylic acid,* $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3(OH){\cdot}CO_2H$. This crystallises in needles, m. p. 166—167°, sublimes when carefully heated, distils with superheated steam, gives an intense blue coloration with ferric chloride in highly dilute alcoholic or aqueous solution, and forms a *dibromide*, $C_{13}H_{16}O_3Br_2$, crystallising in prisms, m. p. 160—161°.

Methyl crotonylidenemalonate, $C_9H_{12}O_4$, obtained in a 39% yield by the action of crotonaldehyde on methyl malonate in presence of piperidine at − 5°, forms a yellow oil with a faint odour, b. p. 130—135°/15 mm., D^{15} 1·1105, n_D^{15} 1·48849.

The *condensation* product of α-methyl-β-ethylacraldehyde and methyl malonate, $C_{11}H_{16}O_4$, b. p. 139—145°/16 mm., is obtained in a 30% yield. When boiled with alcoholic sodium hydroxide, it is converted into *o*-hydroxymesitylenic acid, m. p. 180° (Fittig and Hoogewerff, *Annalen*, 1869, **150**, 333).

Methyl o-*tolylidenemalonate,* $C_{13}H_{14}O_4$, forms white crystals, m. p. 59—60°, b. p. 165—170°/11 mm., and, on hydrolysis, yields *o*-methylcinnamic acid.

Condensation of Crotonaldehyde with Acetone: Crotonylideneacetone.—The action of crotonaldehyde on acetone in aqueous sodium hydroxide leads to the formation of *crotonylideneacetone,*

$$CHMe{:}CH{\cdot}CH{:}CH{\cdot}COMe,$$

in a 23% yield; it is obtained as a mobile, strongly refracting oil with an aromatic odour, b. p. 78—80°/16 mm., D^{15} 0·8990, n_D^{15} 1·51954, is readily oxidised on exposure to air, and forms an *additive compound* with four atoms of bromine. The *oxime*, $C_7H_{11}ON$, crystallises in white needles, m. p. 90—92°, b. p. 124—125°/14 mm.; the *semicarbazone*, $C_8H_{13}ON_3$, crystallises in nacreous leaflets, m. p. 157—158°; the *phenylhydrazone* forms yellow leaflets, m. p. 70—71°. On oxidation with sodium hypochlorite at 70°, the ketone yields chloroform and sorbic acid.

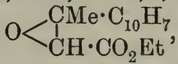
o-*Tolylideneacetone,* $C_{11}H_{12}O$, solidifies when cooled with ice, and melts about the ordinary temperature, forming a colourless, strongly refracting oil, b. p. 136—138°/10 mm. G. Y.

Constitution of Tannin. III. MAXIMILIAN NIERENSTEIN (*Ber.*, 1908, **41**, 77—80. Compare Abstr., 1905, i, 914; 1907, i, 331).—The penta-acetyl tannin, m. p. 203°, may be reduced to the acetyl derivative, m. p. 166°, by means of zinc dust and glacial acetic acid. The latter acetyl compound, *acetyl-leucotannin,* when further acetylated in the presence of pyridine, yields a *hexa-acetyl-leucotannin,* m. p. 159°. Penta-acetyl-leucotannin is not reduced, and penta-acetyl tannin cannot be further acetylated. These observations support the view that tannin is a mixture of digallic acid (tannin) and the corresponding reduction product (leucotannin):

$C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(OH)_2\cdot CO_2H$ (tannin)
$C_6H_2(OH)_3\cdot CH(OH)\cdot O\cdot C_6H_2(OH)_2\cdot CO_2H$ (leucotannin).

The formula for leucotannin contains an asymmetric carbon atom which may account for the optical activity of ordinary tannin.

When oxidised, penta-acetyl tannin gives more ellagic acid, but less rufigallic acid, than does triacetylgallic acid. J. J. S.

Glycidic Esters and Aldehydes in the Naphthalene Series. Georges Darzens (*Compt. rend.*, 1907, **145**, 1342—1343. Compare Abstr., 1905, i, 116; 1906, i, 62, 137, 430; 1907, i, 178, 182, 627).—*Ethyl β-1-naphthyl-β-methylglycidate,*  $O<\begin{matrix}CMe\cdot C_{10}H_7\\ |\\ CH\cdot CO_2Et\end{matrix}$, obtained by the condensation of α-naphthyl methyl ketone with ethyl chloroacetate in the presence of sodium ethoxide, is a colourless, viscous liquid, b. p. 165—170°/4 mm.; the corresponding acid on distillation decomposes into carbon dioxide and α-1-*naphthylpropaldehyde,* $C_{10}H_7\cdot CHMe\cdot CHO$, an amber-coloured liquid with an odour similar to that of hydratropaldehyde, b. p. 131—132°/4 mm.; the *semicarbazone* has m. p. 209—210°.

Ethyl β-2-naphthyl-β-methylglycidate, similarly prepared to the above, is an odourless liquid, b. p. 175—180°/5 mm.; the corresponding *acid* is solid, and yields on distillation α-2-*naphthylpropaldehyde,* m. p. 53°; the *semicarbazone* has m. p. 134—135°.

The *semicarbazones* of α- and αβ-naphthyl methyl ketone have m. p. 232—233° and 235—237° respectively. M. A. W.

Menthazine. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, *Chem.*, 1246—1250. Compare Abstr., 1900, i, 277).—*l*-Menthone, when treated with hydrazine hydrate at the ordinary temperature, forms chiefly *l*-menthazine, m. p. 51°, $[\alpha]_D$ −107·68°; at higher temperatures, or when the mixture is distilled, it forms *d*-menthazine, m. p. 83·5°, $[\alpha]_D$ +64·89° to +85·27°. The latter is also formed when *d*-menthone is employed. The liquid product formed in the action of hydrazine hydrate on *l*-menthone consists of a mixture of *l*- and *d*-menthazines. The production of the *d*-menthazine is due to the isomerisation of *l*-menthazine at higher temperatures. Z. K.

Ketone Derived from β-Hexahydrocarvacrol. Léon Brunel (*Compt. rend.*, 1907, **145**, 1427—1429).—When the β-hexahydrocarvacrol (β-carvacromenthol), obtained by the direct hydrogenation of carvacrol in the presence of reduced nickel (Abstr., 1906, i, 81), is oxidised with chromic acid, it yields the ketone, carvacromenthone, b. p. 221—221·5°, D^0 0·908. The oxime, amine, and two isomeric semicarbazides were prepared, and were found to be identical with the corresponding derivatives of tetrahydrocarvone described by Baeyer (Abstr., 1893, i, 359) and Wallach (Abstr., 1894, i, 44; 1896, i, 101); it follows therefore that β-carvacromenthol (1-methyl-4-*iso*-propyl*cyclo*hexane-2-ol) is identical with tetrahydrocarveol.

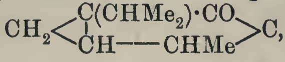
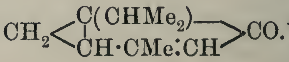
M. A. W.

Components of Ethereal Oils. Constitution of Umbellulone, $C_{10}H_{14}O$. FRIEDRICH W. SEMMLER (*Ber.*, 1907, **40**, 5017—5023).—The physical data for dihydroumbellulone show that it is not a dicyclic derivative belonging to the pinene, camphor, or *dicyclo*-octanone series (compare Tutin, Trans., 1906, **89**, 1104; 1907, **91**, 271). Umbellulone, $C_{10}H_{14}O$, has b. p. 93—98°/10 mm., D^{20} 0·958, n_D 1·4895, α_D $-31·5°$ (100 mm. tube), mol. ref. 45·19. Dihydroumbellulol, $C_{10}H_{18}O$, has b. p. 91—93°/10 mm., D^{20} 0·931, n_D 1·47348, α_D $-27·5°$ (100 mm. tube). β-Dihydroumbellulone, $C_{10}H_{16}O$, has b. p. 83—87°/10 mm., D^{20} 0·928, n_D 1·45862, α_D $-30·5°$ (100 mm. tube).

Dihydroumbellulone forms oxymethylene and benzylidene compounds, showing that the keto-group is adjacent to a CH_2 group. The *oxymethylene* compound has b. p. 105—107°/10 mm., D^{18} 1·001, n_D 1·49097; it yields homotanacetonedicarboxylic acid on oxidation, and gives a violet-red coloration with ferric chloride. The *benzylidene* compound has b. p. 185—188°/9 mm., D^{20} 1·03, n_D 1·574, and solidifies to minute needles, m. p. 81—82°.

The molecular refractions of these compounds are all considerably higher than the calculated values, as is also the case in the tanacetone series.

l-Benzylidene-β-dihydroumbellulone yields, on oxidation, d-*homotanacetonedicarboxylic acid*, m. p. 146—147°, α_D $+2·5°$ (20% solution in 100 mm. tube), which unites with the *l*-homotanacetonedicarboxylic acid from *d*-tanacetone (compare Semmler, Abstr., 1904, i, 176) to form i-*homotanacetonedicarboxylic acid*, m. p. 179°, and crystallising in short needles. The *d*-acid forms a neutral *ethyl* ester, b. p. 148—153°/10 mm., and an oily *acid ethyl* ester.

Dihydroumbellulone is regarded as a tanacetone of the methone series,  $CH_2<\begin{array}{l}C(CHMe_2)\cdot CO\\ \vert\\ CH{-\!-\!-}CHMe\end{array}>C$, whereas umbellulone has a double bond adjacent to the keto-group,  $CH_2<\begin{array}{l}C(CHMe_2){-\!-\!-}\\ \vert\\ CH\cdot CMe{:}CH\end{array}>CO$.*

E. F. A.

Oxygen Derivatives of Camphene. THADDEUS MILOBENDSKI (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, *Chem.*, 1395—1403).—The camphene prepared from *iso*borneol has m. p. 47·5—48·5°, b. p. 159·5°/755 mm., and is optically inactive; that from pinene hydrobromide has m. p. 44—45°, b. p. 159·5°/755 mm., $[\alpha]_D$ $-41°46'$.

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* See also Tutin, *Proc.*, 1908, **24**.

The former, when oxidised with permanganate, yielded only a very small quantity of neutral products, containing a glycol, m. p. 197·5—198·5°, and a trace of acid, having the odour of acetic acid. The glycol obtained from the other camphene has m. p. 181—185°, $[\alpha]_D$ +21°40′; after subliming at 110°, m. p. 156—177°, and when re-sublimed at 96°, m. p. 169—175°. The glycol obtained from diacetylcamphene has m. p. 160—161°. The first glycol, m. p. 197·5—198·5°, when dehydrated, yields camphenilonealdehyde, m. p. 68·5—70°, and a white, resinous *substance* distilling above 300°/15 mm. When the glycol is oxidised with potassium permanganate, it yields camphenilone, m. p. 36—37°, a small quantity of volatile acids, camphenilic acid, m. p. 170—171° (*sodium* salt, $C_{10}H_{15}O_3Na,5H_2O$), and camphenecamphoric acid, m. p. 135—136°. With nitric acid, the glycol yields two *acids*, $C_{10}H_{16}O_2$, m. p. 93·5—94°, $C_{10}H_{16}O_4$, m. p. 191·5—192·5°, *apo*camphoric anhydride, $C_9H_{12}O_3$, m. p. 177·5—178°, a *ketonic acid*, m. p. 235°, the *oxime* of which has m. p. 195—196·5°, and some other crystalline products which could not be isolated. With chromic acid, the glycol yields camphenilone and camphenecamphoric acid.

Camphenecamphoric acid, obtained from either of the two camphenes mentioned above, is optically inactive, and has m. p. 135·5—136°, and distils at 235—237°/10—11 mm., 250—251°/20 mm., but when it is obtained from camphene prepared from borneol chloride it has m. p. 145—146°. The chloroanhydride of camphenecamphoric acid has b. p. 153·5—154·5°/13 mm., but in estimating the chlorine in alcoholic solution the results are too low. It was not found possible to obtain the pure ethyl ester by Fischer's method. The chromate is also described. An attempt was made to determine the constitution of the acid by bromination, then removing hydrogen bromide by means of potassium hydroxide, and, finally, oxidising the unsaturated acids so obtained with potassium permanganate, but without success. One crystalline *unsaturated acid*, m. p. 147·5—149°, was thus isolated; it is readily soluble in water, alcohol, and chloroform. Z. K.

Investigations in the Terpene and Camphor Series. Leo A. Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, *Chem.*, 1324—1343. Compare Abstr., 1905, i, 71, 166).—Since pinene is very unstable, most of its derivatives have a different constitution from the parent substances; consequently, to obtain true derivatives, the xanthogen reaction has been applied, as in this case polymerisation does not occur. Pinocampheol was prepared from pinene by a modification of Wallach's method, and then converted into the xanthogen *derivative*, $C_{10}H_{17}{\cdot}O{\cdot}C{\cdot}S_2Me$, m. p. 60·5—61°; it forms rhombic crystals $[a:b:c = 1{\cdot}3747:1:0{\cdot}97875]$. At 180—190°, it decomposes thus: $C_{10}H_{17}{\cdot}O{\cdot}CS_2Me \longrightarrow C_{10}H_{16} + MeSH + CSO$, yielding inactive pinene; from this it is evident that pinocamphone and pinocampheol are true derivatives of pinene (compare Wallach and Engelbrecht, Abstr., 1906, i, 683).

l-Dihydrocarveol was converted into the *xanthate*, $C_{10}H_{17}{\cdot}O{\cdot}CS_2Me$, which by the action of ammonia yielded the *amide*, $C_{10}H_{17}{\cdot}O{\cdot}CSNH_2$, m. p. 62—63°, $[\alpha]_D^{21}$ −138·89°; it forms rhombic crystals $[a:b:c = 0{\cdot}6548:1:0{\cdot}7058]$. The racemic modification of this amide has

m. p. 95·5—96°, crystallises in small needles, and is much less soluble in organic solvents than the active amides. Methyl dihydrocarveol xanthate decomposes at 180—190° in exactly the same manner as pinocampheol xanthate, forming the *terpene*, $C_{10}H_{16}$, b. p. 172—174°, $n_D^{20·5}$ 1·46972, $D_{20·5}^{20·5}$ 0·8382, $[\alpha]_D$ +131·93°.

The Sachgeisa oil or resin, which is used as a chewing gum by the natives of South Caucasia, when subjected to steam distillation, yields an oil consisting almost wholly of inactive pinene together with a small quantity of active terpene. The resin is analogous with that obtained from the bark of the tree *Pistacia lenticus*, and known as mastic. Z. K.

New Method for the Hydration of Pinene. PHILIPPE BARBIER and VICTOR GRIGNARD (*Compt. rend.*, 1907, **145**, 1425—1427).—When pinene in acetic acid solution is treated with a solution of benzenesulphonic acid, it is converted to the extent of 52·3% into terpineol. For this purpose, freshly-distilled French pinene is dissolved in an equal weight of acetic acid, one-tenth of its weight of a 50% aqueous solution of benzenesulphonic acid added, and the mixture shaken until it becomes homogeneous. After twelve hours, water is added, and the insoluble layer washed, dried, and separated by distillation into two fractions, the first, boiling below 85°/15 mm., consists of unchanged pinene with a small quantity of a terpadiene, b. p. 175—178°, and the second fraction, boiling above 85°/15 mm., after saponification with alcoholic potassium hydroxide at 110—115°, is composed of terpineol, b. p. 100—105°/13 mm., m. p. 35°, together with a small quantity of borneol, fenchyl alcohol, and a viscous substance not identified.

When large quantities of purified pinene are submitted to the above reaction, a hydrocarbon having a lower boiling point than the original pinene can be isolated from the product. M. A. W.

Santene. OSSIAN ASCHAN (*Ber.*, 1907, **40**, 4918—4923).—In addition to *l*-pinene, *l*-camphene, phellandrene, Müller's santene has been isolated from Siberian turpentine and identified by conversion into the nitrosochloride, nitrosite, tribromide (m. p. 77—80°. Müller gives 62—63°), and hydrochloride, as well as by direct comparison with the santene obtained from sandal wood oil (Abstr., 1900, i, 678). It has b. p. 140°, D^{15} 0·8698, $n_D^{19·2}$ 1·4690, and the formula C_9H_{14} is confirmed.

Santenol acetate, $C_9H_{15}·OAc$, prepared by using acetic and sulphuric acids, is a clear liquid, resembling *iso*bornyl acetate in odour, b. p. 215—219°/760 mm., and 88—89°/8 mm., D_4^{20} 0·9871, optically inactive, n_D^{19} 1·45929, thus showing the compound to be saturated.

The santenol, obtained on hydrolysis, is a solid mixture, two-thirds of which has b. p. 195—196°, and the remainder b. p. 196—198°, and the conjecture is made that it is similar to the *iso*borneol-borneol mixture obtained from camphene. By recrystallisation from light petroleum, large, transparent plates, m. p. 97—98°, are obtained. The *phenylurethane* forms long needles, m. p. 61—62°. Oxidation of santenol results in the formation in small quantity of a ketone (*semicarbazone*, m. p. 225—226°).

Santene is also a constituent of oils from *Pinus picea*, *Abies exelsa*, and a Swedish turpentine. W. R.

Russian Turpentine Oil and Russian Pine Tar Oil. IWAN SCHINDELMEISER (*Chem. Zeit.*, 1908, **32**, 8).—Russian turpentine and pine tar oils contain sylvestrene, dipentene, and, in the pinene fraction, nopinene, identified by the formation of the sparingly soluble acid, m. p. 126°, and sparingly soluble sodium salt on oxidation with permanganate. The pine tar oil contains also toluene, cymene, and a quinone-like *substance*, which has a sharp odour, is resinified, becoming yellow, on treatment with sodium hydroxide and metallic sodium, and reacts with hydroxylamine and phenylhydrazine, together with saturated acyclic hydrocarbons, one of which, b. p. 98—99°, is probably a heptane. A sesquiterpene present in Russian pine tar oil is, perhaps, identical with the sesquiterpene occurring together with cadinene in cade oil. G. Y.

Turmeric Oil. HANS RUPE (*Ber.*, 1907, **40**, 4909—4910. Compare Jackson and Menke, Abstr., 1883, 482).—When turmeric oil is boiled with dilute sodium hydroxide, the main product is a substance containing oxygen, b. p. 156°/12 mm., which is probably not identical with Jackson and Menke's turmerol, and does not exhibit the properties of an alcohol, aldehyde, acid, or ketone. When boiled with stronger alkali, it yields an optically active *ketone*, $C_{13}H_{18}O$, b. p. 119—120°/8 mm., which forms a *semicarbazone*, m. p. 119·5—120·5°, an *oxime*, b. p. 159°/11 mm., and well-crystallised condensation products with aromatic aldehydes. The ketone is oxidised by potassium permanganate to terephthalic acid and *p*-methylacetophenone, and yields, by treatment with alkali hypobromite, a *hydroxy-acid*, $C_{12}H_{16}O_3$, m. p. 150°, and an *acid*, $C_{12}H_{16}O_2$, m. p. 33—34°; the latter is oxidised by potassium permanganate to a dicarboxylic *acid*, $C_{12}H_{14}O_4$, m. p. 228°. C. S.

Action of Nitrous Acid on Caoutchoucs. OTTO GOTTLOB (*Zeitsch. angew. Chem.*, 1907, **20**, 2213—2221. Compare Harries, Abstr., 1905, i, 223; this vol., i, 39).—The products obtained by the action of nitrous fumes on crude or purified caoutchoucs vary in composition with the proportion of nitrogen peroxide present in the mixture of nitrogen oxides, but all are more or less impure forms of Harries' nitrosite, $C_{10}H_{15}O_7N_3$. The latter substance can only be obtained in a pure state by strictly following the directions given by Harries (Abstr., 1903, i, 189). The existence of the nitrosate, $C_9H_{16}O_6N_2$, described by Alexander (Abstr., 1905, i, 223; 1907, i, 433; *Zeitsch. angew. Chem.*, 1905, **18**, 164) is doubtful. The same author's statement that carbon dioxide is liberated during the action of nitrous fumes on caoutchouc is correct, but the quantity evolved only corresponds with roughly 0·3% of the total carbon present in the caoutchouc treated. W. H. G.

West African Copals, especially Angola and Cameroon Copals. Alexander Tschirch and H. Rackwitz (*Arch. Pharm.*, 1907, **245**, 415—426. Compare Abstr., 1897, i, 92).—The constants are given of samples of copal from Sierra Leone, Accra, Benin, Loango, Congo, and Benguela.

The Angola copal examined had m. p. 140—170°, acid number 135, saponification number 155, and iodine number 66. The copal was extracted with ether. From the ethereal solution, 1% aqueous ammonium carbonate did not extract anything, but 1% aqueous sodium carbonate extracted : (1) amorphous *angocopalolic acid*, $C_{23}H_{36}O_3$, m. p. 85°, acid number 157, corresponding with monobasicity (the *silver* salt was analysed), saponification number 155, and iodine number 71, corresponding with one double bond, precipitated in alcoholic solution by lead acetate, and (2) a resinous acid not so precipitated. By evaporating the ether and distilling with steam, an *essential oil*, b. p. 140—160°, D 0·853, passed over, whilst yellow, amorphous *α-angocopaloresen*, $C_{30}H_{54}O_6$, or $C_{30}H_{56}O_6$, m. p. 63—65°, remained behind. From the residue of the copal insoluble in ether, alcohol-ether extracted, in addition to traces of angocopalolic acid, yellow *β-angocopaloresen*, $C_{25}H_{38}O_4$, m. p. 220—224°. There remained insoluble in alcohol-ether a substance resembling bassorin, soluble in aqueous sodium hydroxide, and insoluble inorganic silicates. In 100 parts of the drug are contained: angocopalolic and other acids, soluble in ether, 64; essential oil, 2; α-angocopaloresen, 3; acid soluble in ether (?), 5; β-angocopaloresen, 20; substance resembling bassorin, 0·3; ash, 5·7.

The Cameroon copal examined had m. p. 105—125°, acid number 126, saponification number 157, and iodine number 68. After extraction with ether for three months, aqueous ammonium carbonate did not extract anything from the ethereal solution, but 1% aqueous sodium carbonate extracted: (1) amorphous *cameroocopalolic acid*, $C_{21}H_{36}O_3$, m. p. 98—100°, acid number 160, corresponding with monobascity (the *silver* salt was analysed also), saponification number 188, and iodine number 76·5, corresponding with one double bond, precipitated in alcoholic solution by lead acetate; and (2) a resinous acid not so precipitated. By evaporating the ether and distilling with steam, a yellow *essential oil*, b. p. 145—155°, D 0·830, was driven over, whilst viscous *α-cameroocopaloresen* remained behind. From the residue of the copal insoluble in ether, alcohol-ether extracted *β-cameroocopaloresen*, $C_{25}H_{38}O_4$, m. p. 220—224°. There remained insoluble in alcohol-ether a *substance* resembling bassorin, soluble in aqueous sodium hydroxide, and an insoluble residue largely inorganic in character. In 100 parts of the drug are contained: cameroocopalolic and other acids, 70; essential oil, 2; α-cameroocopaloresen, 3; β-cameroocopaloresen, 20; substance resembling bassorin, 3; ash, 2. C. F. B.

Heerabol Myrrh. Oscar von Friedrichs (*Arch. Pharm.*, 1907, **245**, 427—457. Compare Köhler, Abstr., 1890, 1317; Tucholka, Abstr., 1897, i, 584; and especially Tschirch and Bergmann, Abstr., 1906, i, 197; Lewinsohn, Abstr., 1906, i, 972).—Commercial samples of

Myrrha electa were examined, and consisted of yellowish-brown to reddish-brown pieces with a waxy, translucent fracture.

The following substances were isolated from it: (1) a volatile essential oil (8·8%), viscid, yellow to yellowish-green, D^{15} 1·011, n_D^{20} 1·5359, $[\alpha]_D^{20}-73{\cdot}9°$, acid number 6·15, and ester number 47·6. From this oil, there were separated formic and acetic acids and a crystalline *acid*, m. p. 159°, which was not volatile with steam, *m*-cresol, cuminaldehyde and cinnamaldehyde, and the crystalline, monobasic *myrrholic acid*, $C_{17}H_{22}O_5$, m. p. 236° (of which the amorphous *silver*, *lead*, and *copper* salts were analysed), and the sesquiterpene, *heerabolene*, $C_{15}H_{24}$, b. p. 130—136°/16 mm., D^{20} 0·943, n_D^{20} 1·5125, a_D^{20} 14°10′ in 100 mm. tube, the molecular refraction indicating a tricyclic sesquiterpene; this yielded a crystalline *dihydrochloride*, $C_{15}H_{24},2HCl$, m. p. 98—99°.

(2) That part of the resin which was soluble in light petroleum yielded some acetic acid when submitted to dry distillation.

From that part of the drug insoluble in light petroleum, but soluble in ether, the following constituents were separated: *a-commiphoric acid*, $C_{14}H_{18}O_4$, m. p. 201—203°, is monobasic; *β-commiphoric acid*, m. p. 205°, has the same formula and basicity; *γ-commiphoric acid*, $C_{17}H_{22}O_5$, m. p. 169—172°, is monobasic; all three acids are amorphous, yellow to brown, cannot be acetylated, and do not contain methoxy-groups. *a-Heerabo-myrrhol*, $C_{18}H_{26}O_5$, m. p. 248—250°, forms a *diacetyl* derivative of m. p. 228° (decomp.), and is precipitated from an alcoholic solution by lead acetate; *β-heerabo-myrrhol*, $C_{20}H_{26}O_6$, m. p. 168°, forms a *diacetyl* derivative. *Commiphorinic acid*, $C_{28}H_{36}O_8$, m. p. 135°, is brown, amorphous, and monobasic; the barium salt is insoluble in water and alcohol. A yellow *alcohol*, $C_{14}H_{22}O_2$, b. p. 264°, which forms a *monoacetyl* derivative of b. p. 243°, and is volatile with steam; and the non-volatile, yellow, amorphous *heeraboresen*, $C_{42}H_{56}O_8$, m. p. 100—102°, which contains one methoxyl group.

The part of the drug insoluble both in light petroleum and in ether was soluble in aqueous sodium carbonate. It was separated into (1) brown, amorphous, monobasic *a-heerabo-myrrhololic acid*, $C_{15}H_{22}O_7$, m. p. 220—225°, of which the amorphous *silver* and *lead* salts were analysed, but no acetyl derivative could be prepared; it is precipitated in alcoholic solution by lead acetate, and (2) *β-myrrhololic acid*, $C_{25}H_{32}O_6$, m. p. 187—190°, not so precipitated, brown, amorphous, and monobasic, of which the *silver* salt was analysed.

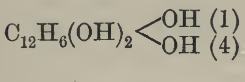
The *gum* had $[\alpha]_D+23{\cdot}8°$ in 2% aqueous solution, and was mixed with an enzyme of the oxydase group; when oxidised with nitric acid, it yielded mucic acid, and when distilled with hydrochloric acid, furfuraldehyde; hence it probably contained galactose and arabinose.

No bitter principle was detected, but the volatile oil has a biting, unpleasant taste. C. F. B.

Baptisia Glucosides. IV. ψ-Baptisin. K. Gorter (*Arch. Pharm.*, 1907, **245**, 561—572. Compare Abstr., 1897, i, 627; 1898, i, 39; 1906, i, 973).—The presence of one hydroxyl group in ψ-baptigenin has been confirmed by the preparation of the *benzoate*, $C_{15}H_9O_5Bz$, crystallising in small, white needles, m. p. 216°.

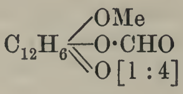
The substance obtained by heating the sodium derivative of ψ-baptigenin with ethyl iodide and alcohol (compare Abstr., 1906, i, 973) is now shown to have the composition $C_{14}H_{10}O_4$, and is named *ψ-baptigin*; it crystallises in small, colourless plates, m. p. 172° (not 169°, as previously stated). It yields neither an acetyl nor a benzoyl derivative, and, consequently, cannot contain a hydroxyl group. Since the formation of ψ-baptigin is accompanied by the production of formic acid, it follows that ψ-baptigenin must have the partially structural formula $C_{14}H_8O_4{:}CH{\cdot}OH$. No ψ-baptigin results on heating sodium ψ-baptigenin with ethyl alcohol alone, and in the presence of ethyl iodide only one-half of the ψ-baptigenin is converted into ψ-baptigin. What probably happens in the latter case is as follows: part of the sodium ψ-baptigenin is converted into the ethyl ether, which is then hydrolysed, with the formation of ψ-baptigin and ethyl formate: $C_{14}H_8O_4{:}CH{\cdot}OEt + H_2O = C_{14}H_{10}O_4 + H{\cdot}CO_2Et$. The ethyl formate, together with ethyl alcohol, reacts with more sodium ψ-baptigenin, forming ethyl ether, sodium formate, and ψ-baptigenin: $C_{14}H_8O_4{:}CH{\cdot}ONa + H{\cdot}CO_2Et + EtOH = C_{14}H_8O_4{:}CH{\cdot}OH + H{\cdot}CO_2Na + OEt_2$.

The substance, $C_{13}H_{12}O_4$, previously described (Abstr., 1898, i, 39), is now shown to be *methylbaptigenetin*, and is formed together with formic acid on hydrolysing ψ-baptigin with alcoholic potassium hydroxide. It yields on acetylation two acetyl derivatives, colourless, rhomboidal crystals, m. p. about 123°, and colourless, rectangular crystals, m. p. 148°. These could not be isolated in a pure state, but it is probable from an analysis of the mixture that the compounds formed are *triacetylmethylbaptigenetin* and *acetylanhydromethylbaptigenetin*. From the above facts, together with those previously published (*loc. cit.*), it follows that baptigenetin must have the partially structural formula (I), and ψ-baptigin the formula (II). Since ψ-baptigenin, when heated with potassium hydroxide solution, yields baptigenetin, formic acid, and methyl alcohol, it is probable that it has the formula (III):



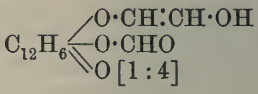
$$C_{12}H_6(OH)_2 < \begin{matrix} OH\ (1) \\ OH\ (4) \end{matrix}$$

(I.)



$$C_{12}H_6 \begin{cases} OMe \\ O{\cdot}CHO \\ O\ [1:4] \end{cases}$$

(II.)



$$C_{12}H_6 \begin{cases} O{\cdot}CH{:}CH{\cdot}OH \\ O{\cdot}CHO \\ O\ [1:4] \end{cases}$$

(III.)

When heated under pressure with 5% hydrochloric acid at 200° for two hours, methylbaptigenetin yields a small quantity of a substance which has the properties of catechol. It is possible therefore that baptigenetin is a derivative of diphenylene oxide. W. H. G.

Chitin. Theodor R. Offer (*Biochem. Zeitsch.*, 1907, 7, 117—127).—Chitin, prepared from the carapace of the lobster by successive treatment with dilute hydrochloric acid, boiling 10% potassium hydroxide, potassium permanganate, and sodium hydrogen sulphite, was hydrolysed by 70% sulphuric acid at the ordinary temperature, and yielded two amorphous substances of the composition $C_{14}H_{26}O_{10}N_2$. One of these is *acetyldiglucosamine*, m. p. 194° (decomp.), soluble in water, and optically inactive. The other is insoluble in water, gives a reddish-brown coloration with iodine, and is regarded as a polymeride of the former substance.

In acetyldiglucosamine, one amino-group is probably acetylated, whilst the amino-group of the second glucosamine molecule is condensed with the aldehyde group of the first.

Chitin itself is regarded as a highly polymerised acetyldiglucosamine.

G. B.

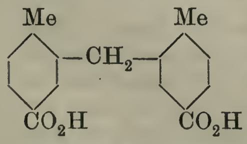
Solanin from the Seeds and Flowers of Solanum Tuberosum. Amedeo Colombano (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 683—690; 755—762. Compare Oddo and Colombano, Abstr., 1905, i, 455).—From a study of the physical and chemical characters of various samples of solanin, the author draws the conclusion that the latter exhibits properties varying with the source from which it is obtained. Thus solanin extracted from *Solanum tuberosum* differs essentially from that isolated from *S. sodomæum*, the two products yielding different solanidins when treated with boiling dilute hydrochloric acid.

T. H. P.

Phylloxanthin. Leon Marchlewski (*Biochem. Zeitsch.*, 1907, **7**, 282—285. Compare Abstr., 1907, i, 69, 71, 784, 787, 865, 866, 867, 948).—Polemical. The identity of certain chlorophyll derivatives described by Tsvett and Willstätter is discussed, and the former's spectroscopic results with phylloxanthin are described as incorrect.

W. D. H.

Rottlerin. Franz Herrmann (*Arch. Pharm.*, 1907, **245**, 572—585. Compare A. G. Perkin, Trans., 1893, **63**, 975; 1895, **67**, 230; Telle, Abstr., 1906, i, 973; 1907, i, 435; Thoms, Abstr., 1907, i, 545).—Perkin's *iso*rottlerin is considered to be impure rottlerin; his formula, $C_{33}H_{30}O_9$, for the latter compound is, however, confirmed. Rottlerin in alkaline solution yields, on oxidation with hydrogen peroxide at 75°, cinnamic and benzoic acids. 2 : 4 : 6-Trihydroxytoluene results on decomposing rottlerin with concentrated potassium hydroxide solution at 150°; the same compound is also formed together with 2 : 4 : 6-trihydroxy-*m*-xylene, acetic acid, and a tarry *substance* by heating a solution of rottlerin in 15% aqueous sodium hydroxide a short time with zinc dust. The tarry substance is oxidised in alkaline solution by hydrogen peroxide, with the formation of a dibasic *acid*, $C_{17}H_{16}O_4$, crystallising in slender, colourless needles, m. p. 184°; the *silver* salt, $C_{17}H_{14}O_4Ag_2$, and *ethyl* ester, crystallising in needles, m. p. 115°, were prepared. The acid is converted by cold fuming nitric acid into a *dinitro*-derivative, $C_{17}H_{14}O_4(NO_2)_2$, crystallising in small, colourless, rhombic plates, m. p. 284°; the corresponding *amine* forms hone-shaped crystals. The *dibromo*-derivative $C_{17}H_{14}O_4Br_2$, results on treating the acid with bromine in glacial

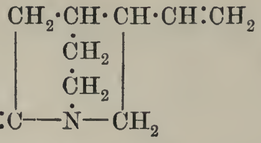


acetic acid; it forms stellate crystals, m. p. 172—173°. It is probable that the acid has the formula given on p. 99. W. H. G.

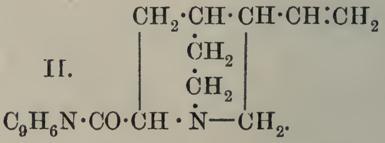
Cinchona Alkaloids. VIII. Constitution of Cinchonine. Paul Rabe [with Otto Buchholz] (*Ber.*, 1908, 41, 62—70).—The base, $C_{19}H_{20}ON_2$ (Abstr., 1907, i, 954), obtained by oxidising cinchonine with chromic acid, is termed *cinchoninone* in order to indicate its relation to tropinone and codeinone. It is amphoteric in character, and exhibits keto-enolic tautomerism, since it yields both an oxime and an *O*-benzoyl derivative. It is readily reduced, and under special conditions can be converted back into cinchonine; under normal conditions, however, a rupture of the molecule occurs during the reduction.

Nitrous acid (amyl nitrite) decomposes the ketonic base, yielding cinchonic acid and an oxime, $C_9NH_{13}{:}N\cdot OH$, a reaction which is analogous to the formation of diacetylmonoxime from ethyl methylacetoacetate. The presence of the grouping $-CO\cdot CH<$ is thus established. The oxime, when hydrolysed, yields meroquinenine, and, assuming Koenig's formula for this compound, the following constitutional formulæ are deduced for the oxime, $C_9NH_{13}\cdot NOH$, and cinchoninone:

I.



$$\begin{array}{l} CH_2\cdot CH\cdot CH\cdot CH{:}CH_2 \\ \quad | \qquad \dot{C}H_2 \quad | \\ \quad | \qquad \dot{C}H_2 \quad | \\ HO\cdot N{:}C — \dot{N} — CH_2 \end{array}$$



$$\begin{array}{l} \qquad CH_2\cdot CH\cdot CH\cdot CH{:}CH_2 \\ \text{II.} \qquad | \qquad \dot{C}H_2 \quad | \\ \qquad\quad | \qquad \dot{C}H_2 \quad | \\ C_9H_6N\cdot CO\cdot CH\cdot \dot{N} — CH_2. \end{array}$$

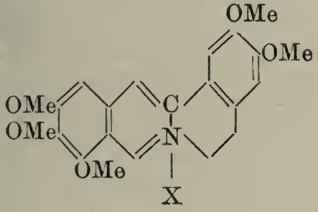
Cinchoninoneoxime, $C_{19}H_{21}ON_3$, obtained by the action of free hydroxylamine on the ketone in a strongly alkaline solution, forms a pale yellow, amorphous powder, m. p. 105—110°. It yields a *methiodide*, $C_{19}H_{21}ON_3,MeI$, which has no definite m. p.; it begins to soften at 135°, and decomposes at 145—150°. The *benzoyl* derivative, $C_{26}H_{24}O_2N_2$, of the base crystallises from light petroleum in colourless needles, m. p. 131°; it is readily hydrolysed by alkalis, and possesses very feeble basic properties. Cinchoninone methiodide also yields a *benzoyl* derivative, $C_{26}H_{24}O_2N_2,MeI$, which is hydrolysed when boiled with alcohol.

A 75% yield of *α′-oximino-β-vinyl-quinuclidine* (formula I above) is obtained by the action of amyl nitrite and sodic ethoxide on the ketone; it crystallises from ethyl acetate or a mixture of ether and light petroleum (b. p. 40°) in colourless prisms or needles, m. p. 146—147°, and yields a *methiodide*, $C_9H_{14}ON_2,MeI$, m. p. 224° (decomp.). J. J. S.

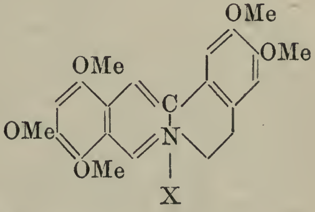
Alkaloids and Bitter Principles of Calumba Root. VIII. Karl Feist (*Arch. Pharm.*, 1907, 245, 586—637. Compare Gadamer, Abstr., 1903, i, 50; 1906, i, 976).—Three alkaloids have been obtained from calumba root, namely, columbamine, jateorrhizine, and palmatine. Günzel's work on columbamine (Abstr., 1906, i, 976) has been confirmed; further investigation has shown that columbamine contains a hydroxyl group in addition to the four $-OMe$ groups; columbamine iodide consequently has the partly structural formula: $C_{17}H_9NI(OMe)_4{\cdot}OH$.

Jateorrhizine iodide, which has the empirical formula $C_{20}H_{20}O_5NI$, is found to contain three $-OMe$ groups and two hydroxyl groups, so that the formula may be written $C_{17}H_9NI(OMe)_3(OH)_2$; in fact, columbamine is a monomethyl ether of jateorrhizine, since the monomethyl ether of columbamine is identical with the dimethyl ether of jateorrhizine. Both columbamine and jateorrhizine, also their methyl ethers, are very similar to berberine, yielding colourless tetrahydro-derivatives, &c. The methyl ether of columbamine yields, on oxidation with potassium permanganate, corydaldine (Dobbie and Lauder, Trans., 1902, 81, 145) together with a trimethoxy-*o*-phthalic acid. The acid, which was not obtained in a pure state, melted at almost the same temperature as gallocarboxylic acid trimethyl ether (3 : 4 : 5-trimethoxy-*o*-phthalic acid), but crystallised in a different form. Should the two acids on further investigation be proved to be identical, then salts of columbamine methyl ether must be represented by formula I. If not, the only other trimethoxy-*o*-phthalic acid possible is 3 : 4 : 6-trimethoxy-*o*-phthalic acid, and salts of columbamine methyl ether would then have the formula II:

I.



II.



The third alkaloid, palmatine, only small quantities of which are present in calumba root, closely resembles berberine; it contains four OMe groups, but no hydroxyl group, and the iodide has the formula $C_{17}H_{10}O_2NI(OMe)_4$; the relationship existing between this alkaloid and columbamine is not yet known.

The discovery of a second bitter principle in calumba root, named provisionally "bitter principle II," led to an investigation of columbin. The value obtained for the mol. wt. of the latter compound by the boiling- and freezing-point methods varied considerably with the solvent employed; consequently, the mol. wt. of this substance is still unknown (compare Ulrich, Abstr., 1907, i, 331). Owing to the similarity of the two substances, it is possible that the columbin hitherto investigated has been contaminated with "bitter principle II."

Columbamine nitrate, $C_{21}H_{22}O_8N_2,2\frac{1}{2}H_2O$, crystallises in lemon-yellow needles, m. p. 232°; the *platinichloride*, $(C_{21}H_{21}O_5N)_2,H_2PtCl_6$, is a yellow powder, m. p. 238° (decomp.); the *aurichloride* forms slender needles, m. p. 220° (decomp.). Concentrated solutions of columbamine sulphate or nitrate yield on treatment with strong aqueous potassium hydroxide the inner *anhydride* of columbamine, which crystallises in violet-black prisms, commences to melt at 190°, and decomposes above this temperature. Tetrahydrocolumbamine is most readily prepared by the reduction of columbamine nitrate; the *sulphate* crystallises in white, silky needles; the *chloride* forms a colourless, crystalline powder, commences to melt at 150°, and is completely molten at 215°. All attempts to separate tetrahydrocolumbamine into its optically active components were unsuccessful. Columbamine chloride reacts with benzoyl chloride, yielding a *substance*, obtained as a light yellow, crystalline powder, m. p. 152°. In pyridine solution, however, a *substance*, obtained as a light yellow powder, m. p. 212—213°, is formed. Acetyl chloride reacts with columbamine chloride in pyridine, forming a *substance* (acetyl derivative ?) which crystallises in slender, yellow needles, m. p. 220° (decomp.).

None of these substances was obtained in a pure state. That columbamine contains a hydroxyl group is shown by the preparation of the methyl ether; the *iodide* of *columbamine methyl ether*,

$$C_{17}H_9NI(OMe)_5,$$

results on heating columbamine iodide with potassium hydroxide, methyl alcohol, and methyl iodide in a sealed tube at 100°; it crystallises in prisms, m. p. 238—240°; the *sulphate* results on treating columbamine iodide with methyl sulphate in the presence of alkali; the *nitrate* crystallises in slender, light yellow prisms, m. p. 236° (decomp.). A concentrated solution of the sulphate, when treated with 50% aqueous potassium hydroxide, yields the *ψ-form* of columbamine methyl ether; it crystallises in light yellow prisms, m. p. 136°. Columbamine methyl ether yields with chloroform an *additive* compound, $C_{22}H_{23}O_5N,CHCl_3$, forming small, light grey crystals, m. p. 182°, and with acetone an *additive* compound, obtained as a dirty yellow, fine, crystalline powder.

Tetrahydrocolumbamine methyl ether is obtained by reducing the nitrate of columbamine methyl ether; it crystallises in colourless prisms, m. p. 148°.

Columbamine methyl ether yields, on oxidation with aqueous potassium permanganate, corydaldine, a *trimethoxyphthalic acid*, $C_6H(OMe)_3(CO_2H)_2$, crystallising in colourless, slender needles, m. p. 200°, and an *acid* containing nitrogen, crystallising in colourless prisms, m. p. 200—202°. The composition of the latter acid is not yet known; its *hydrochloride* forms colourless needles, m. p. 208° (decomp.), and *aurichloride* crystallises in slender, light yellow needles, m. p. 188° (decomp.). In order to compare the above trimethoxyphthalic acid with gallocarboxylic acid methyl ether (3 : 4 : 5-*trimethoxyphthalic acid*), this compound was prepared by treating the acid with diazomethane in ethereal solution, and hydrolysing the dimethyl ester so formed with alcoholic potassium hydroxide; it crystallises in small, colourless, rhombic plates, m. p. 195°. Gallocarboxylic acid yields on treatment with methyl sulphate, in the presence of alkali, a substance, probably a *monomethyl ether*, $C_8H_5O_6(OMe)$, crystallising in colourless needles, m. p. 251°.

Jateorrhizine iodide, $C_{20}H_{20}O_5NI,H_2O$, crystallises in reddish-yellow needles, m. p. 208—210°; the corresponding *chloride* crystallises from water with $\frac{1}{2}H_2O$ in light yellow needles, m. p. 206°, and from alcohol with $1H_2O$ in copper-coloured needles, m. p. 206°; the *sulphate* forms brownish-yellow prisms; the *nitrate* crystallises in glistening, golden-yellow needles, m. p. 225° (decomp.). The latter salt yields, on reduction, *tetrahydrojateorrhizine*, $C_{20}H_{23}O_5N$, crystallising in colourless needles, m. p. 206°. Jateorrhizine iodide yields on methylation a *dimethyl ether* identical with columbamine methyl ether iodide.

Palmatine iodide, $C_{17}H_{10}O_2NI(OMe)_4$, remains undissolved on treating the mixture of iodides of the alkaloids obtained from calumba root with aqueous sodium hydroxide; it crystallises in slender, yellow needles, m. p. 238—240° (decomp.). The corresponding *nitrate*, $C_{21}H_{22}O_6N\cdot NO_3,1\frac{1}{2}H_2O$, forms slender, lemon-yellow needles, m. p. 238—240°. Reduction of this salt leads to the formation of *tetrahydropalmatine*, $C_{21}H_{25}O_6N$, crystallising in colourless leaflets, m. p. 145°; the *aurichloride*, $C_{21}H_{25}O_6N,HAuCl_4$, forms small, cinnamon-brown crystals.

An alcoholic extract of calumba root yields on evaporation a mixture of orange-red prisms and nodular aggregates of yellow crystals. The orange-red substance was found on investigation to be jateorrhizine chloride with $2H_2O$. The yellow substance was found to be a mixture of columbamine nitrate with some "bitter principle II." The latter substance crystallises in prisms, m. p. 246° (decomp.), and is a lactone. In agreement with the statement of Ulrich (*loc. cit.*), columbic acid was not detected in the alcoholic extract. W. H. G.

***iso*Sparteine, an Isomeride of Sparteine.** CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1907, **145**, 1343—1345. Compare this vol., i, 44).—iso*Sparteine*, $C_{15}H_{26}N_2$, obtained by treating the hydriodide (*loc. cit.*) with sodium hydroxide, is a colourless, almost odourless oil, b. p. 177·5—177° (corr.)/16·5 mm., $[\alpha]_D$ $-25·01°$ in 10% alcohol solution, D_4^{17} 1·02793, n_D^{17} 1·53319; the *dihydrochloride* is a deliquescent, crystalline solid; the *platinichloride*, $C_{15}H_{26}N_2,H_2PtCl_6,1·5H_2O$, forms silky tufts of crystals, blackens at 230°, and decomposes at 257—260°; the *sulphate* forms a thick syrup, soluble in water or the alcohols, and insoluble in acetone or ether; the hydriodide, m. p. 202° (corr.), has α_D $-33·2°$ in 5·5% methyl-alcoholic solution; the *dihydriodide*, $C_{15}H_{26}N_2,2HI,H_2O$, is a crystalline salt, optically inactive, and yields the hydriodide on treatment with sodium carbonate; the *picrate*, $C_{15}H_{26}N_2,2C_6H_3O_7N_3$, crystallises in needles, and has m. p. 178° (corr.). *iso*Sparteine methiodide (*loc. cit.*) cannot be obtained by the action of methyl iodide on the base; it is a crystalline salt, m. p. 232° (corr.), $[\alpha]_D$ $-18·39°$ in 1·25% aqueous solution, or $-16·79°$ in 6·2% methyl-alcoholic solution; the hydriodide,

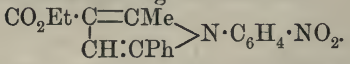
$$C_{15}H_{26}N_2,MeI,HI,H_2O,$$

loses its water of crystallisation at 145°, decomposes with loss of MeI at 220—225°, and has α_D $-11·80°$ in aqueous solution.

*iso*Sparteine is a saturated ditertiary base; it does not reduce acid permanganate solution, and on treatment with hydrogen iodide does not yield methyl iodide; the compound therefore contains methyl groups associated with nitrogen (Herzig and Meyer, Abstr., 1896, i, 68).

M. A. W.

Synthesis of Pyrrole and Piperazine Derivatives from the Three Nitroanilines. WALTHER BORSCHE and J. CAMPHER TITSINGH (*Ber.*, 1907, **40**, 5008—5017).—The three nitroanilines, dissolved in acetic acid, react with ethyl phenacylacetate to give pyrrole derivatives of the following constitution:



$$\begin{matrix}CO_2Et\cdot C{=}CMe\\ CH{:}CPh\end{matrix}>N\cdot C_6H_4\cdot NO_2.$$

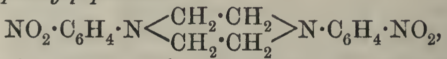
The yield in the case of the meta- and para-compounds is about 70%, but is much less from the ortho-derivative. Paal (*Habilitationsschrift*, Würzburg, 1890) found that *o*-nitroaniline did not react with ethyl phenacylacetate.

Ethyl-5-*phenyl*-1-m-*nitrophenyl*-2-*methylpyrrole*-3-*carboxylate* forms citron-yellow, rhombic plates, m. p. 146—147°; zinc chloride and hydrogen chloride reduce it to the corresponding base, *ethyl*-5-*phenyl*-1-m-*aminophenyl*-2-*methylpyrrole*-3-*carboxylate*, crystallising in colourless needles, m. p. 145°, which, when diazotised and combined with phenol, forms an orange *hydroxyazo*-compound.

The corresponding p-*nitrophenylpyrrole* derivative forms yellowish-red, thick plates, m. p. 116—117°, and the p-*aminophenylpyrrole* compound, colourless, matted needles, m. p. 161—162°. The o-*nitrophenylpyrrole* compound gives yellow needles, m. p. 96—97°, and the o-*aminophenyl* derivative, m. p. 109°, decomposes rapidly in the atmosphere, becoming red.

s-Bis-*m*-nitrophenylaminoethane, $C_2H_4(NH\cdot C_6H_4\cdot NO_2)_2$ (compare Gattermann and Hager, Abstr., 1884, 1142), prepared by the interaction of *m*-nitroaniline and ethylene dibromide in presence of sodium acetate at 150°, whereby, contrary to the experience with aniline, no cyclic compound is formed, has m. p. 206—208°. The corresponding *tetra-amine* crystallises in colourless, glistening plates or flat needles, m. p. 107°, and forms a *tetra-acetate* separating in colourless needles, m. p. 272°.

N-*Di*-m-*nitrophenylpiperazine*



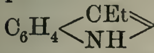
$$NO_2\cdot C_6H_4\cdot N<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>N\cdot C_6H_4\cdot NO_2,$$

prepared by further heating of nitrophenylaminoethane with ethylene dibromide, forms brownish-yellow needles, m. p. 220°. *s*-Bis-*p*-nitrophenylaminoethane (compare Jedlicka, Abstr., 1893, i, 699) is obtained in small quantity only by this reaction. Still worse is the yield in the case of the *o*-compound (compare Jedlicka, *loc. cit.*), due to the decrease in basicity and less tendency to form quaternary ammonium compounds.

m-Nitroaniline reacts with chloroacetic acid to form a mixture of m-*nitrophenylglycine*, $NO_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2H$, a yellow compound, m. p. 158—159°, and m-*nitrophenylglycine*-m-*nitroanilide*,

$$NO_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2,$$

a brown, crystalline powder, m. p. 201—202°. *p*-Nitroaniline reacts similarly to give *p*-nitrophenylglycine, m. p. 225°, and p-*nitrophenylglycine*-p-*nitroanilide*, m. p. 260°. *o*-Nitroaniline, on the other hand, gave only traces of *o*-nitrophenylglycine. E. F. A.

Catalytic Action of Finely-divided Metals on Nitrogen Compounds. MAURICE PADOA and C. CHIAVES (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 762—766. Compare Abstr., 1907, i, 722).—When carbazole is heated at 200—220° for twelve to eighteen hours in hydrogen under 8—10 atmospheres pressure, and in presence of reduced nickel, the following products are obtained: (1) a base, which yields a platinichloride, m. p. 213° (decomp.); and (2) 2 : 3-*diethylindole* (?),  $C_6H_4<\substack{CEt\\NH}>CEt$, which crystallises from light petroleum in scales, m. p. 95°, and forms a dark-red *picrate*, m. p. 172—173°, and a *picryl chloride* compound, $C_{12}H_{15}N,C_6H_2Cl(NO_2)_3$, m. p. 117°. T. H. P.

The Melting Point of Phenylhydrazine and of Certain Osazones. Emil Fischer (*Ber.*, 1908, **41**, 73—77).—Phenylhydrazine was purified by fractional distillation at 15—20 mm., solidification and removal of the liquid portion (repeated four times), crystallisation from anhydrous ether at low temperatures, and finally by distillation under 0·5 mm. pressure. The melting point of the product, as determined by stirring with a normal thermometer, was found to be +19·6°.

For ordinary purposes, it is sufficient to crystallise the base once or twice from its own volume of pure ether and then to distil once under a pressure of 10—20 mm. The base should be coloured pale yellow, and should dissolve in ten times its vol. of a mixture of 50% acetic acid (1 part) and water (9 parts). In the preparation of osazones, it is an advantage to use the old method, namely, a mixture of 2 parts of phenylhydrazine hydrochloride and 3 of sodium acetate, as the sodium chloride thus formed facilitates the formation of the osazone. The phenylhydrazine hydrochloride must be colourless, and if coloured should be crystallised from alcohol.

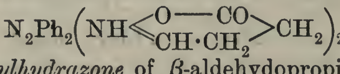
The melting points of osazones depend to a certain extent on the manner in which the substances are heated. The previous melting points are confirmed, namely, 205° or 208° (corr.) for phenylglucosazone, when the osazone is heated fairly rapidly. Tutin's value of 217° (*Proc.*, 1907, **23**, 250) could not be obtained.

Certain phenylhydrazones, for example, pyruvic acid phenylhydrazone, which decompose when heated, melt differently, according to the rate at which they are heated. J. J. S.

Action of Phenylhydrazine on Dibromopyrotartaric Acid. Fritz Fichter and Markus Guggenheim [and, in part, Ludwig Brasch] (*J. pr. Chem.*, 1907, [ii], **76**, 545—551).—The action of phenylhydrazine on dibromopyrotartaric acid in hot aqueous solution leads to the formation of the phenylhydrazone of β-aldehydopropionylphenylhydrazide (Perkin and Sprankling, Trans., 1899, **75**, 11; Ellinger, Abstr., 1904, i, 639). As Reitter and Bender have found this substance to be formed also by the action of phenylhydrazine on aconic acid (Abstr., 1905, i, 669), the interaction of phenylhydrazine and dibromopyrotartaric acid takes place probably in two stages, the first consisting of the formation of phenylhydrazine hydrobromide and aconic acid. When boiled with mercuric oxide in alcoholic solution, the phenylhydrazone-hydrazide is oxidised, forming the *diphenyldihydrotetrazone* of β-aldehydopropionylphenylhydrazide,

$$N_2Ph_2(N{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}N_2H_2Ph)_2,$$

which separates in yellowish- or reddish-brown crystals, m. p. 122°, gives with concentrated sulphuric acid a brown coloration becoming blue and finally violet, and when heated with phenylhydrazine on the water-bath is reduced to the phenylhydrazone-hydrazide; the diphenyldihydrotetrazone is formed also, but in smaller yields, if a current of air is passed through a hot alcoholic solution of the phenylhydrazone-hydrazide. When treated with concentrated hydrochloric acid in the cold, the diphenyldihydrotetrazone is hydrolysed, forming the *diphenyldihydrotetrazone* of β-aldehydopropionic acid, which crystallises in colourless leaflets, m. p. 160°. As this substance has not an acid reaction and does not react with barium carbonate, but forms a readily soluble, yellowish-white *salt* when boiled with aqueous baryta, it is considered to have the constitution:



$$N_2Ph_2\left(NH\Big<\begin{matrix}O\text{——}CO\\ CH\cdot CH_2\end{matrix}\Big>CH_2\right)_2.$$

The p-*bromophenylhydrazone* of β-aldehydopropionyl-*p*-bromophenylhydrazide, $C_6H_4Br\cdot NH\cdot N{:}CH\cdot CH_2\cdot CH_2\cdot CO\cdot N_2H_2\cdot C_6H_4Br$, prepared by the action of *p*-bromophenylhydrazine on dibromopyrotartaric acid, crystallises in white needles, m. p. 206°.

The p-*tolylhydrazone* of β-aldehydopropionyl-*p*-tolylhydrazide, $C_{18}H_{22}ON_4$, crystallises in glistening leaflets, m. p. 217°, and, on oxidation by means of a current of air in alcoholic solution, yields the *di*-p-*tolyldihydrotetrazone*, $C_{36}H_{42}O_2N_8$, crystallising in yellow needles, m. p. 153°. G. Y.

Hofmann's Reaction with Amides and Hydrazine Derivatives of Carbonic Acid. August Darapsky (*J. pr. Chem.*, 1907, [ii], 76, 433—466. Compare Schestakoff, Abstr., 1905, i, 332).—A detailed account of work previously published (Abstr., 1907, i, 729). The following facts are new.

Benzoylsemicarbazide is best prepared by the action of potassium cyanate on benzoylhydrazide in glacial acetic acid solution; it is not oxidised to the azocarbonamide by chromic acid, and when treated with sodium hypochlorite yields nitrogen, carbon dioxide, and benzoic acid.

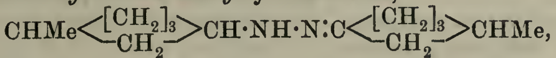
p-Bromophenylazocarbonamide sinters at 160°, m. p. 177° (m. p. 165°: Hantzsch and Glogauer, Abstr., 1898, i, 78). The action of sodium hypochlorite on *p*-methyl-, *p*-bromo-, and *p*-nitro-phenylazocarbonamide leads to the formation of the corresponding azoimides together with small amounts of the *s*-azo-compounds.

β-Naphthylazoimide (Culmann and Gasiorowski, Abstr., 1889, 1156) crystallises in white prisms, m. p. 31—32°.

as-Dibenzyl- and *as*-diethyl-carbamides do not yield the *as*-disubstituted hydrazines when treated with sodium hypochlorite.

Benzoylhydrazide is converted by the hypochlorite into benzylidenebenzoylhydrazone, or dibenzoylhydrazide, and azodibenzoyl, depending on the conditions of the reaction. G. Y.

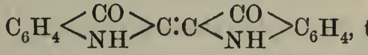
Conversion of the Azine of 1-Methyl*cyclo*hexone-3-one into 1-Methyl*cyclo*hexyl-3-hydrazine. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1907, 39, *Chem.*, 1240—1245. Compare Abstr., 1900, i, 277, 333).—The azine is prepared by the action of hydrazine hydrate on methyl*cyclo*hexanone, b. p. 170—172°/770 mm., α_D +1·52° (100 mm.), but when the azine is decomposed with hydrochloric acid it yields methyl*cyclo*hexanone, b. p. 169·5°/750 mm., and $a_D + 12·20°$. The alcoholic solution of the azine is reduced readily by sodium, forming methyl*cyclo*hexylamine, b. p. 154—155°, $a_D - 1·70°$ (100 mm.), and *methyl*cyclo*hexahydrazone methyl*cyclo*hexanone*,

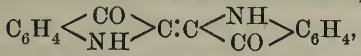


$$CHMe<\substack{[CH_2]_3\\CH_2}>CH\cdot NH\cdot N:C<\substack{[CH_2]_3\\CH_2}>CHMe,$$

b. p. 214°/90 mm., a thick, pale greenish-yellow liquid, $a_D - 26·54°$ (100 mm.). When treated with dilute acids, it decomposes, forming methyl*cyclo*hexanone and a salt of methyl*cyclo*hexylhydrazine, which with alkalis forms the free methyl*cyclo*hexylhydrazine, b. p. 209·5—210·5°/760 mm., D_0^{20} 0·9274, n_D^{20} 1·4786, $[a]_D - 9·66°$. It is a colourless liquid, becoming thick, but not crystallising, at $-20°$. It combines with hydrochloric and sulphuric acids, and also with benzaldehyde and menthone. The *compound*, $NHPh\cdot CS\cdot NH\cdot NH\cdot C_7H_{13}$, crystallises in long needles, m. p. 135°, $[a]_D - 17·66°$. Methyl*cyclo*hexane has n_D^{20} 1·4228.
Z. K.

Stereochemistry of Indigotin. K. George Falk and John M. Nelson (*J. Amer. Chem. Soc.*, 1907, 29, 1739—1744).—From the consideration of a number of compounds containing a double bond, and existing in two stereoisomeric modifications, it is inferred that, if one of the isomerides is coloured, the other will either be colourless or of a different colour from the first.

Indigotin has the constitution:  $C_6H_4<\substack{CO\\NH}>C:C<\substack{CO\\NH}>C_6H_4$, the carbonyl groups being in the *cis*-position, since the compound yields only a mono-oxime (Thiele and Pickard, Abstr., 1898, i, 493). There is a possibility of the existence of a *trans*-isomeride,



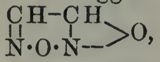
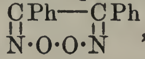
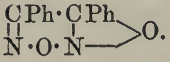
$$C_6H_4<\substack{CO\\NH}>C:C<\substack{NH\\CO}>C_6H_4,$$

which would be expected to have a different colour from that of ordinary indigo.

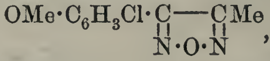
Liebermann and Dickhuth (Abstr., 1892, 480) have described a red diacetylindigotin. It is suggested that a stereoisomeric change takes place during the formation of this compound, and that it has the *trans*-configuration. Similarly, the *trans*-structure is proposed for other red indigotin derivatives. Liebermann and Dickhuth's work has been repeated, and their results confirmed. A general scheme is given of the relations between the acetyl derivatives of indigo and the best methods of passing from one compound to another. Liebermann and Dickhuth regarded α-diacetylindigo-white as containing the group $\cdot CO\cdot\overset{|}{C}H\cdot\overset{|}{C}H\cdot CO\cdot$, and the β-compound as containing the group, $\cdot C(OH):\overset{|}{C}\cdot\overset{|}{C}:C(OH)\cdot$. It is considered more likely, however, that the α-form is internally compensated, and that the β-form is a racemic mixture capable of resolution into its optically active components.
E. G.

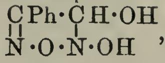
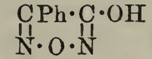
Electrolytic Reduction of Indigotin. Henri Chaumat (*Compt. rend.*, 1907, 145, 1419—1421).—Indigotin can be readily reduced by electrolytic hydrogen when it is intimately associated with the cathode of a cell in which sodium carbonate solution is undergoing electrolysis.

For this purpose, the indigotin, in a fine state of division, mixed with a slightly coarser powder of graphite is piled round a stick of carbon in a linen bag, and forms the cathode of an electrolytic cell charged with sodium carbonate solution and provided with a porous diaphragm to separate the two electrodes. The hydrogen liberated at the cathode during the electrolysis reduces the indigotin to indigo-white, which is dissolved by the equivalent of sodium hydroxide simultaneously formed. The introduction of the porous diaphragm to protect the reduced indigotin from the action of electrolytic oxygen liberated at the anode greatly increases the resistance of the cell, and can be dispensed with if a solution of alkali or alkaline earth sulphite, hydrogen sulphite, or sulphide is added to the bath, these salts being more readily oxidised than the indigo-white. M. A. W.

Constitution of the Glyoxime Peroxides. HEINRICH WIELAND and LEOPOLD SEMPER (*Annalen*, 1907, **358**, 36—70. Compare Wieland, Abstr., 1903, i, 764; 1904, i, 54).—The results of the investigation described in this paper have led the authors to suggest for the so-called glyoxime peroxide the structural formula:  $\begin{array}{l}CH{-}CH\\ \| \qquad | \\ N{\cdot}O{\cdot}N{-}{-}\end{array}{>}O$, which is an oxide of furazan and is termed furoxan. The nomenclature of the derivatives of glyoxime peroxide is altered accordingly; thus diphenylglyoxime peroxide,  $\begin{array}{l}CPh{-}{-}CPh\\ \| \qquad\quad \| \\ N{\cdot}O{\cdot}O{\cdot}N\end{array}$, becomes diphenylfuroxan,  $\begin{array}{l}CPh{\cdot}CPh\\ \| \qquad | \\ N{\cdot}O{\cdot}N{-}{-}\end{array}{>}O$.

The furoxans are readily converted into the corresponding furazans when heated with phosphorus pentachloride. In this manner, phenylfurazan is prepared from phenylfuroxan. *Diphenylfurazan*, $C_{14}H_{10}ON_2$, obtained from diphenylfuroxan, crystallises in colourless prisms, m. p. 94°, yields an odour of benzonitrile and phenylcarbimide when heated, and remains unchanged on treatment with Caro's acid.

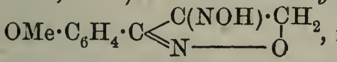
Chloroanisylmethylfurazan,  $\begin{array}{l}OMe{\cdot}C_6H_3Cl{\cdot}C{-}{-}CMe\\ \qquad\qquad\quad \| \qquad \| \\ \qquad\qquad\quad N{\cdot}O{\cdot}N\end{array}$, is formed by the action of phosphorus pentachloride on anisylmethylfuroxan; it crystallises in white plates, m. p. 79—81°.

Phenylfuroxan (Scholl, Abstr., 1891, 317) crystallises in colourless plates, m. p. about 95° (slight decomp.), is stable in a desiccator, yields benzonitrile, but, contrary to Scholl's statement, not benzaldehyde on prolonged boiling with alcohol, dissolves unchanged in concentrated sulphuric acid or boiling concentrated hydrochloric acid, and does not give Liebermann's reaction or a coloration with ferric chloride. When treated with dilute sodium hydroxide, phenylfuroxan rapidly dissolves, evolving an odour of benzonitrile and phenylcarbylamine, and forming a yellow solution which must contain *oximinobenzoylformhydroxamic acid*, $NOH{:}CPh{\cdot}C(NOH){\cdot}OH$, as it gives with ferric chloride an intense brownish-red coloration stable towards mineral acids, and with copper acetate a dirty green, slimy precipitate, which after solution in an acid gives the coloration with ferric chloride. When treated with ice-cold alcoholic potassium hydroxide or aqueous sodium carbonate and ether, phenylfuroxan undergoes isomerisation, which is explained with the aid of the hypothetical intermediate product,  $\begin{matrix}\text{CPh}\cdot\text{CH}\cdot\text{OH}\\ \| \qquad | \\ \text{N}\cdot\text{O}\cdot\text{N}\cdot\text{OH}\end{matrix}$, and leads to the formation of *hydroxyphenylfurazan*,  $\begin{matrix}\text{CPh}\cdot\text{C}\cdot\text{OH}\\ \| \qquad \| \\ \text{N}\cdot\text{O}\cdot\text{N}\end{matrix}$; this crystallises in colourless needles, m. p. 110—111° (decomp.), dissolves in aqueous alkalis, and can for the greater part be regained by immediate acidification, but is gradually decomposed by the alkali, forming the preceding hydroxamic acid and benzonitrile. The hydroxyfurazan gives a brown coloration with alcoholic ferric chloride, forms a crystalline *acetate*, and reacts with phosphorus pentachloride with explosive violence, yielding a crystalline *product*.

Oximinobenzoylamidoxime, $\text{NOH:CPh}\cdot\text{C(NOH)}\cdot\text{NH}_2$, prepared by treating phenylfuroxan in ethereal solution with ice-cold aqueous ammonia, or in small amount by prolonged boiling of oximinobenzoyl cyanide with hydroxylamine, crystallises in colourless leaflets, m. p. 154°, is soluble in alkalis or mineral acids, and gives an olive-brown coloration with ferric chloride. The *dibenzoyl* derivative, $C_{22}H_{17}O_4N_3$, forms leaflets, m. p. 175—176°.

Crystalline, substituted *amidoximes* are formed from phenylfuroxan by the action of phenylhydrazine, $\text{NOH:CPh}\cdot\text{C(NOH)}\cdot\text{NH}\cdot\text{NHPh}$, m. p. 173° (decomp.), or aniline, $\text{NOH:CPh}\cdot\text{C(NOH)}\cdot\text{NHPh}$, m. p. about 180° (decomp.).

When boiled with water, phenylfuroxan yields benzonitrile oxide, which polymerises forming diphenylfuroxan, formhydroxamic acid, and an odour of benzonitrile.

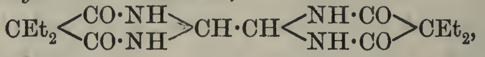
The transformation of furoxans into *iso*nitroso*iso*oxalines has been described by Tönnies (Abstr., 1881, 167) and by Angeli (Abstr., 1892, 1198). iso*Nitrosoanisyl*iso*oxazoline*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\!<\!\begin{matrix}\text{C(NOH)}\cdot\text{CH}_2\\ \text{N}\text{———}\text{O}\end{matrix}$, formed by boiling anisylmethylfuroxan with methyl-alcoholic potassium hydroxide, crystallises in colourless needles, m. p. 172° (decomp.), is soluble in aqueous sodium carbonate, and is decomposed when treated with alkalis. The *benzoyl* derivative, $C_{17}H_{14}O_4N_2$, crystallises in white needles, m. p. 143°. The action of methyl sulphate on the solution obtained on heating anisylmethylfuroxan with methyl-alcoholic potassium hydroxide leads to the formation of a *methyl* derivative of *iso*nitrosoanisyl*iso*oxazoline, $C_{11}H_{12}O_3N_2$, crystallising in needles, m. p. 107—108°.

The disubstituted furoxans are less reactive than the monosubstituted, and are not attacked by ammonia, aniline, or phenylhydrazine even at high temperatures under pressure. Diphenylfuroxan remains almost unchanged on prolonged boiling with alcoholic potassium hydroxide. With magnesium organic compounds, the furoxans form labile *additive* products, from which they separate unchanged on treatment with water. The *additive* compound of magnesium ethyl iodide and anisylmethylfuroxan is an insoluble, yellow substance.

The *ψ-nitrosite*, $(N_2O_2)[CH(C_6H_4\cdot OMe)\cdot CH_2\cdot NO_2]_2$, formed from *p*-methoxystyrene, is obtained as a white, crystalline powder, decomp.

107°, gives the reactions for ψ-nitrosites, and on distillation in a current of steam yields nitroanisylethylene and the *nitro-oxime* of *p*-methoxystyrene, $OMe\cdot C_6H_4\cdot C(NOH)\cdot CH_2\cdot NO_2$. This crystallises in colourless needles, m. p. 112°, decomp. 135°, dissolves in aqueous alkalis, and is precipitated by acids. This ψ-nitrosite and nitro-oxime differ from the homologous compounds derived from anethole in that they do not yield the corresponding furoxan. G. Y.

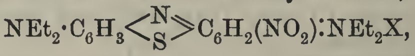
Reduction of Diethylthiobarbituric Acid. ALFRED EINHORN and HEINRICH VON DIESBACH (*Ber.*, 1907, **40**, 4902—4903).—The reduction of diethylthiobarbituric acid by sodium amalgam leads to the formation mainly of diethylmalonamide; the by-products are 4 : 6-dihydroxy-5 : 5-diethyl-2 : 5-dihydropyrimidine (compare Tafel and Thompson, this vol., i, 58), which is isolated in the form of the double *salt* with mercuric chloride, $C_{18}H_{14}O_2N_3,HgCl_2$, m. p. 215—218°, and *bisdiethylmalonyltetra-aminoethane*,



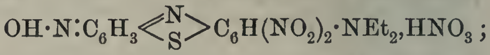
$$CEt_2<\substack{CO\cdot NH\\CO\cdot NH}>CH\cdot CH<\substack{NH\cdot CO\\NH\cdot CO}>CEt_2,$$

m. p. 340°, which separates from dilute alcohol in white prisms containing $2H_2O$. C. S.

Thiazines. II. Derivatives of Tetraethylthionine. ROBERT GNEHM and ALFRED SCHINDLER (*J. pr. Chem.*, 1907, [ii], **76**, 471—488. Compare Gnehm and Walder, this vol., i, 63).—Tetraethylthionine (ethylene-blue) is more reactive than methylene-blue, as, whilst the action of the theoretical amount of nitric acid in glacial acetic acid solution leads to the formation of nitroethylene-blue,



$$NEt_2\cdot C_6H_3<\substack{N\\S}>C_6H_2(NO_2){:}NEt_2X,$$

the nitration readily proceeds further to the formation of the nitrate of a dinitronitroso-base,  $OH\cdot N{:}C_6H_3\ll\substack{N\\S}>C_6H(NO_2)_2\cdot NEt_2,HNO_3$; the position of the nitro-groups in this base has not been determined. The paper contains an account of these substances and their reduction products.

Tetraethylthionine is prepared by the action of sodium thiosulphate and hydrochloric acid on nitrosodiethylaniline hydrochloride and treatment of the product with diethylaniline hydrochloride, zinc chloride, and sodium dichromate in boiling aqueous solution. The *zincochloride* is salted out as a blackish-blue powder, and, when gently heated with nitric acid in acetic acid solution, yields *dinitro*iso*nitrosodiethylaminothiazine nitrate*, $C_{16}H_{15}O_5N_5S,HNO_3,\frac{1}{2}H_2O$, which separates from alcohol in green crystals; the *hydrobromide*,

$$C_{16}H_{15}O_5N_5S,HBr,\tfrac{1}{2}H_2O,$$

prepared by the action of hydrobromic acid and methyl alcohol on the nitrate, is obtained in green crystals or as a brown powder, forms bluish-red dichroic solutions which, with the exception of the aqueous solution, are fluorescent, and with concentrated sulphuric acid gives a malachite-green coloration, becoming blue and finally rose-red on dilution. The free *base*, formed by the action of sodium hydroxide on the hydrobromide, is obtained as a brown, flocculent precipitate, detonates when heated on platinum, is insoluble in alkalis, and again forms the dye on solution in hydrochloric acid. It gives with phenylhydrazine in acetic acid solution a brownish-yellow precipitate, with ferric chloride a blood-red coloration, with potassium ferricyanide a flesh-red solution, with phenol and concentrated sulphuric acid a green solution, becoming bluish-red when poured into dilute sodium hydroxide, and with aniline in methyl-alcoholic solution a violet coloration. The *hydrochloride* is crystalline. In Formanek's spectroscope, the aqueous solution of the dye shows a line at $\lambda = 573$, the alcoholic solution shows a line at $\lambda = 573 \cdot 4$, and an absorption band in the blue; on addition of ammonia, the lines disappear, but the band persists.

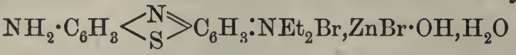
Reduction of the dye with stannous chloride and hydrochloric acid leads to the formation of the *hydrochloride* of the leuco-base, $C_{16}H_{21}N_5S,3HCl$, which separates from aqueous hydrogen chloride in crystals containing $5H_2O$, or from methyl-alcoholic hydrogen chloride in white crystals, $C_{16}H_{21}N_5S,3HCl,3CH_4O$. The light brown *base*, m. p. above 300°, is readily oxidised by air. The dye, prepared by oxidation of the leuco-base with ferric chloride, is isolated as the *zincochloride*, $C_{16}H_{19}N_5S,2HCl,ZnCl_2,\frac{3}{4}CH_4O$. It forms green to brown solutions in water, alcohols, or acids; the spectrum of the alcoholic solution has strong absorption in the red, or, after addition of ammonia, a broad band in the green.

Ethylene-green (*nitroethylene-blue, nitrotetraethylthionine*) is isolated as the *zincobromide*, $C_{20}H_{24}O_2N_4SBr,\frac{1}{2}ZnBr_2,2H_2O$; it dissolves in water, alcohols, or acetic acid, forming a bluish-green solution, gives with concentrated sulphuric acid a dirty blue coloration, becoming reddish-brown, violet, and, finally, bluish-green on addition of water, and with fuming nitric acid a reddish-violet, becoming deep blue on dilution. Addition of sodium hydroxide to the aqueous solution leads to the formation of a reddish-violet coloration, and a precipitate which yields the original dye on treatment with hydrochloric acid; potassium ferrocyanide in aqueous solution gives a light green coloration. The spectrum of the aqueous solution has a broad line at $\lambda = 639 \cdot 7$, and that of the alcoholic solution a broad line at $\lambda = 672$. The *hydriodide* crystallises in green needles.

Aminoethylene-blue, prepared by reduction of ethylene-green with stannous chloride and oxidation of the product with ferric chloride, is isolated as the *zincobromide*, $C_{20}H_{27}N_4SBr,\frac{1}{2}ZnBr_2,1\frac{1}{2}H_2O$. It forms deep blue solutions, gives with concentrated sulphuric acid a reddish-brown, with concentrated hydrochloric acid a yellow, or with fuming nitric acid a reddish-violet, coloration, becoming violet to bluish-violet on dilution, and yields a brown precipitate with sodium hydroxide. The spectrum of the alcoholic solution has a line about $\lambda = 623 \cdot 8$, and strong absorption in the red.

Bromoethylene-blue is formed by the action of bromine on ethylene-blue nitrate in glacial acetic acid solution; the *zincobromide*, $C_{20}H_{26}N_3SBr,HBr,\frac{1}{2}ZnBr_2,H_2O$, was analysed. The dye forms deep blue solutions, and gives with concentrated sulphuric acid an apple-green, with concentrated hydrochloric acid a bluish-green, and with fuming nitric acid a dark brown, coloration, becoming blue to violet-blue on dilution. On addition of sodium hydroxide, the aqueous solution becomes violet, and when heated turbid; on addition of ammonia, the solution becomes reddish-violet and fluorescent, but blue when heated. With sodium hydroxide, the alcoholic solution gives a cherry-red precipitate. The spectrum of the aqueous solution has a broad line at $\lambda = 670$, and a minor line at $\lambda = 624$; after addition of potassium hydroxide, the broad line has $\lambda = 676$, and the minor line $\lambda = 614 \cdot 8$.

The action of alcoholic ammonia on ethylene-blue nitrate at 145—150° leads to the formation of as-*diethylthionine*, which on oxidation and treatment with zinc bromide yields the *zincobromide*,



$NH_2\cdot C_6H_3{<}\overset{N}{\underset{S}{}}{>}C_6H_3{:}NEt_2Br,ZnBr\cdot OH,H_2O$; this loses H_2O at 80—90°/35 mm. The dye is readily soluble, forming deep blue solutions, gives a reddish-brown *product* with fuming nitric acid, and a reddish-violet precipitate with sodium hydroxide, becoming blue on addition of hydrochloric acid, and is readily reduced to the leuco-base by stannous chloride. Ammonia deepens the shade of the dye, but on heating precipitates the base; potassium ferrocyanide in acetone solution gives a light green precipitate. The aqueous solution gives a spectrum with a line at $\lambda = 676$, the alcoholic solution a line at $\lambda = 662$, and strong absorption on the right. G. Y.

Thiazines. III. Derivatives of Alkylated Benzylanilines. ROBERT GNEHM and ALBERT SCHÖNHOLZER (*J. pr. Chem.*, 1907, [ii], 76, 489—508. Compare preceding abstract; Scholtz, Rohde, and Bosch, Abstr., 1904, i, 992).—Attempts to prepare simple thionines from benzylmethyl- and benzylethyl-aniline were unsuccessful, but, on the other hand, thiazines have been prepared from the sulphonic acids of these bases. The thiazines so obtained and a number of derivatives of benzylmethyl- and benzylethyl-aniline are described.

The *sulphate* of *as*-benzylethyl-*p*-phenylenediamine,

$$CH_2Ph\cdot NEt\cdot C_6H_4\cdot NH_2,H_2SO_4,$$

has m. p. 146—148° (decomp.).

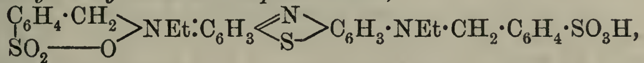
Benzylmethyl-p-*nitrosoaniline*, $NO\cdot C_6H_4\cdot NMe\cdot CH_2Ph$, separates from benzene in steel-blue crystals, m. p. 52—53°; the *hydrochloride* forms a yellow, crystalline precipitate, m. p. 138°. The *diamine*, prepared by reduction of benzylmethyl-*p*-nitrosoaniline, is obtained as a black oil, and forms a *sulphate* crystallising in long, white needles.

Benzylethylanilinesulphonic acid, $NEtPh\cdot CH_2\cdot C_6H_4\cdot SO_3H,H_2O$, prepared by heating benzylethylaniline with sulphuric acid at 110—120°, crystallises in prisms, sinters at 160—170°, m. p. about 190°. The crystalline *barium*, $(C_{15}H_{16}O_3NS)_2Ba,4H_2O$, and *potassium*,

$$C_{15}H_{16}O_3NSK,$$

salts were analysed. The oxidation of the sulphonic acid with chromic acid leads to the formation of only small amounts of azobenzene and traces of benzoic acid. When heated with potassium hydroxide at 240—300°, the potassium sulphonate yields p-*hydroxybenzylethylaniline*, $NEtPh\cdot CH_2\cdot C_6H_4\cdot OH$, m. p. 62—63°, which does not form a rhodamine with phenol. The *nitroso*-derivative, prepared from the sulphonic acid or its potassium salt, is very soluble, forms a green, or in presence of mineral acids an orange-red, solution, and yields a green, amorphous precipitate with lead acetate. On reduction with zinc dust and sulphuric acid, it forms an *amino-sulphonic acid*, which is formed also by reduction of the dark red, amorphous *azo-sulphonic acid*, prepared by coupling diazobenzene chloride and benzylethylanilinesulphonic acid in alkaline solution; the amino-sulphonic acid cannot be isolated either in the free state or as a salt.

Dibenzyldiethylthioninedisulphonic acid,



$$\begin{matrix}C_6H_4\cdot CH_2\\ SO_2\text{——}O\end{matrix}\!>\!NEt{:}C_6H_3\!<\!\begin{matrix}N\\ S\end{matrix}\!>\!C_6H_3\cdot NEt\cdot CH_2\cdot C_6H_4\cdot SO_3H,$$

prepared from benzylethylnitrosoanilinesulphonic acid by reduction with zinc dust and hydrochloric acid, and successive treatment of the product with sodium thiosulphate and dichromate, is identical with commercial thiocarmine. It is obtained as a bluish-black, amorphous powder, is readily soluble in water or alcohol, is precipitated by sulphuric acid, and gives with concentrated hydrochloric acid a green coloration, becoming blue on dilution. The *leuco*-compound, $C_{30}H_{31}O_6N_3S_3$, formed by reduction of the dye with zinc dust, separates as a yellow, flocculent precipitate on addition of sulphuric acid.

The derivatives of benzylmethylaniline are prepared in the same manner as those of benzylethylaniline.

Benzylmethylanilinesulphonic acid, $C_{14}H_{15}O_3NS$, is obtained as a crystalline powder, readily soluble in water; the *barium*,

$$(C_{14}H_{14}O_3NS)_2Ba,2H_2O,$$

and *potassium*, $C_{14}H_{14}O_3NSK$, salts are described.

p-*Hydroxybenzylmethylaniline*, $C_{14}H_{15}ON$, is obtained as a crystalline mass, m. p. 40—41°.

The *nitroso*-derivative of benzylmethylanilinesulphonic acid, prepared by the action of amyl nitrite on the sulphonic acid in glacial acetic acid solution, is obtained as a reddish-brown, crystalline powder; the *product* formed on reduction of this with zinc dust and sulphuric acid is not the *p*-amino-sulphonic acid.

Dibenzyldimethylthioninedisulphonic acid and its *salts* are readily soluble, and separate only as resins. The *leuco*-compound forms a yellow, flocculent precipitate, which decomposes, becoming black when dried in a vacuum.

m-*Nitrobenzylmethylaniline*, $C_{14}H_{14}O_2N_2$, prepared by nitration of benzylmethylaniline by Groll's method (Abstr., 1886, 347), crystallises from alcohol in yellow leaflets, m. p. 51—52°; the *picrate*, m. p. 112—113°. Oxidation of the nitro-base leads to the formation of *m*-nitrobenzoic acid, whilst reduction with stannous chloride and hydrochloric acid leads to the formation of m-*aminobenzylmethylaniline*, which is isolated in the form of its *acetyl* derivative, $NMePh\cdot CH_2\cdot C_6H_4\cdot NHAc$, crystallising in colourless leaflets, m. p. 88°.

Reduction of *m*-nitrobenzylethylaniline and treatment of the product with acetic anhydride leads to the formation of the *acetyl* derivative, $NEtPh\cdot CH_2\cdot C_6H_4\cdot NHAc$, crystallising in leaflets, m. p. 96°. G. Y.

Reduction of Azo-compounds by Means of Sodium Hyposulphite. HARTWIG FRANZEN and P. STIELDORF (*J. pr. Chem.*, 1907, [ii], **76**, 467—471. Compare Grandmougin, Abstr., 1907, i, 850).—

The reduction of an azo-compound, such as helianthin, to two primary amine molecules by means of sodium hyposulphite might take place according to the equation: (I) $NMe_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot SO_3Na + 2Na_2S_2O_4 + 4H_2O = NMe_2 \cdot C_6H_4 \cdot NH_2 + NH_2 \cdot C_6H_4 \cdot SO_3Na + 4NaHSO_3$, or (II) $NMe_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot SO_3Na + Na_2S_2O_4 + 3H_2O =$

$$NMe_2 \cdot C_6H_4 \cdot NH_2 + NH_2 \cdot C_6H_4 \cdot SO_3Na + NaHSO_3 + NaHSO_4.$$

The authors have employed two methods to determine by which reaction the reduction takes place.

As 1 mol. of sodium hyposulphite requires 6 atoms, but 1 mol. of sodium sulphite only 2 atoms, of iodine when titrated, the product of reaction (I) must reduce two-thirds, but that of (II) only one-third, of the iodine required for the titration of the same amount of the original sodium hyposulphite solution. The results obtained with helianthin and *p*-sulphobenzeneazo-*α*-naphthol show that the reaction takes place according to equation (I). The same result is obtained by determining the amount of sulphuric acid in the hyposulphite solution before and after the reduction; only a very slight increase is found, whereas according to equation (II) each mol. of hyposulphite must yield 1 mol. of sulphuric acid. G. Y.

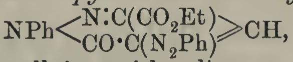
Action of Diazobenzene on Glutaconic Acid and Ethyl Glutaconate. Ferdinand Henrich and W. Thomas (*Ber.*, 1907, 40, 4924—4930).—When glutaconic acid is treated with diazobenzene chloride (2 mols.), *formazylacrylic acid*,

$$NHPh \cdot N:C(N:NPh) \cdot CH:CH \cdot CO_2H,$$

is obtained, accompanied by the evolution of carbon dioxide, crystallising from alcohol in reddish-brown, felted needles, m. p. 199° (decomp.). The *sodium* and *potassium* salts are sparingly soluble; the *silver* salt is dark coloured. The *ethyl* ester, $C_{18}H_{18}O_2N_4$, crystallises in long, slender, dark red needles, m. p. 123°, and is not identical with the formazyl compound previously obtained from ethyl glutaconate and diazobenzene chloride (Abstr., 1902, i, 422). This is now shown to be *ethyl γ-phenylazoglutacononate-phenylhydrazone*,

$$CO_2Et \cdot C(N \cdot NHPh) \cdot CH:C(N:NPh) \cdot CO_2Et,$$

as it readily loses alcohol on boiling its alcoholic solution, forming *ethyl* 1-*phenyl*-5-*benzeneazo*-6-*pyridazone*-3-*carboxylate*,



$$NPh{<}\begin{matrix} N:C(CO_2Et) \\ CO \cdot C(N_2Ph) \end{matrix}{\gg}CH,$$

which crystallises in small, brownish-yellow crystals, m. p. 163—164°. The conclusion that the azohydrazone has the constitution ascribed to it, is supported by the fact that ethyl *α*-methylglutaconate does not give a corresponding derivative with diazobenzene chloride.

With ethyl glutaconate, the diazo-salts from *o*- and *p*-toluidine and chloro- and bromo-anilines give similar derivatives to diazobenzene; the tolyl compounds are deep dark red in colour, and the others are yellowish-red. W. R.

Action of Nitrous Acid on Proteins. Zaccaria Treves and Giovanni Salomone (*Biochem. Zeitsch.*, 1907, 7, 11—23).—Nitrous acid acting on proteins at 0° produces ill-defined substances, which the authors regard as diazo-compounds. The group of the protein molecule concerned in diazotisation is not the same as that which is concerned in the fixation of labile sulphur, or in the combination with formaldehyde. The diazo-compounds show all the characteristic protein reactions, although somewhat slowly and less clearly. After precipitation of the diazo-compounds, no proteins remain in solution. On boiling with water and alkali, the diazo-compounds form proteins, which give a violet biuret reaction. The biuret reaction can scarcely depend on the presence of the complex $CO{\cdot}NH_2$, since this group would be destroyed by the action of nitrous acid. G. B.

Studies on Enzymes. I. Quantitative Measurement of Protein Hydrolysis by "Formaldehyde Titration." S. P. L. Sörensen (*Biochem. Zeitsch.*, 1907, 7, 45—101).—The existing methods for estimating the extent of protein hydrolysis are arbitrary and unsatisfactory. A rational method must attempt the measurement of the quantity of carboxyl- and amino-groups formed during the hydrolysis. This is best done by titrating the carboxyl group with alkali after the aminic function has been abolished by formaldehyde according to Schiff's method (Abstr., 1903, i, 232). The reversibility of this reaction and other circumstances render the employment of certain precautions necessary to ensure accuracy. The indicator must show an end point with as high a concentration of hydroxyl ions as possible; hence phenolphthalein or thymolphthalein (preferable in many cases) must be employed. The end point is not indicated by the appearance of a faint pink coloration, but the titration must be continued until the solution has the same strong red colour as a test solution which is prepared for comparison by adding a few drops of *N*/5 baryta to a dilute formaldehyde solution. The latter has been neutralised previously, so as to give only a faint pink colour with phenolphthalein, and by the addition of the baryta acquires the pronounced red colour which is desired.

Under these conditions, the amount of amino-acid found (in a pure *N*/10 solution) amounts on the average to 98% of the actual amount present. This applies to a large number of mono-, di-, and oxy-amino-acids; only in the case of phenylalanine and tyrosine is a considerably smaller amount found than that actually present.

The ratio between the extents of protein hydrolysis, as measured by this method and by precipitation with tannic acid, is generally greater than 1; at least in the early stages, formaldehyde titration indicates a greater degree of hydrolysis than tannic acid precipitation.

After the addition of formaldehyde, uric acid can be titrated sharply as a monobasic acid. G. B.

Hydrolysis of the Globulin from the Almond (Amandin). Hydrolysis of the Proteins of Maize. Hydrolysis of Gliadin from Rye. Thomas B. Osborne and Samuel H. Clapp (*Amer. J. Physiol.*, 1908, 20, 470—476, 477—493, 493—499).—The following table gives the main results in percentages:

	Amandin.	Gliadin (rye).	Gliadin (wheat).	Hordein (barley).	Zein (maize).	Alkali-soluble protein of maize.
Glycine	0·51	0·13	0·02	absent	absent	0·25
Alanine	1·40	1·33	2·00	0·43	2·23	not isolated
Valine	0·16	not isolated	0·21	0·13	0·29	not isolated
Leucine	4·45	6·30	5·61	5·67	18·60	6·22
Proline...............	2·44	9·82	7·06	13·73	6·53	4·99
Phenylalanine ...	2·53	2·70	2·35	5·03	4·87	1·74
Aspartic acid	5·42	0·25	0·58	not isolated	1·41	0·65
Glutamic acid......	23·14	33·81	37·33	36·33	18·28	12·72
Serine	(?)	0·06	0·13	not isolated	0·57	not isolated
Tyrosine	1·12	1·19	1·20	1·67	3·55	3·78
Arginine	11·85	2·22	3·16	2·16	1·16	7·06
Lysine...............	0·70	absent	absent	absent	absent	2·93
Histidine............	1·58	0·39	0·61	1·28	0·43	3·00
Ammonia	3·70	5·11	5·11	4·87	3·61	2·12
Tryptophan	present	present	present	present	absent	present
Cystine	—	not determined	0·45	not determined	not determined	—
Total	59·00	64·31	65·81	71·32	61·53	45·44

The amino-acids absent in zein are present in the alkali-soluble protein of maize, so that the mixture yields all the amino-acids usually obtained from proteins.

The gliadin of wheat and rye are probably identical, but the differences between it and hordein and zein are noteworthy. These three proteins are all soluble in alcohol, and form a group characterised by their high content of glutamic acid, protein, and ammonia, their low content of arginine and histidine, and absence of lysine. Zein also lacks tryptophan and glycine. W. D. H.

Fatty Acids of Protein Putrefaction and Optically Active Valeric and Hexoic Acids. Carl Neuberg and E. Rosenberg (*Biochem. Zeitsch.*, 1907, 7, 178—190. Compare Abstr., 1906, i, 923).—One kilo. of casein yielded on putrefaction 117 grams of fatty acids. More than one-third of these consisted of butyric acid, which is considered to be derived from glutamic acid, since this acid occurs abundantly among the amino-acids formed in the hydrolysis of casein. Somewhat smaller quantities of formic, valeric, and hexoic acids were obtained, and still smaller yields of acetic, propionic, and a decoic acid. The valeric acid fraction had a rotation indicating the presence of 18% of *d*-α-methylbutyric acid, and the hexoic acid fraction probably contained 46% of β-methylvaleric acid (derived from *iso*leucine). Similar results were obtained with putrefied gelatin. G. B.

Conversion of Optically Inactive Triolein into an Optically Active Glyceride and an Optically Active Acid. Carl Neuberg and E. Rosenberg (*Biochem. Zeitsch.*, 1907, 7, 191—198).—The authors have repeated and confirmed Neuberg's work on the diglyceride of dibromostearic acid (Abstr., 1906, i, 923).

Julius Lewkowitsch (*Chem. Zeit.*, 1908, 32, 54—55) ascribes the optical activity of Neuberg and Rosenberg's products to the introduction of optically active ricinus oil with the lipase employed in the hydrolysis of the glyceride. G. Y.

Organic Chemistry.

Mechanism of Chemical Reactions. Intermediate Products and Intermediate Structures. Marc Tiffeneau (*Bull. Soc. chim.*, 1907, [iv], 1, 1221—1227).—A reply to Freundler (*ibid.*, 216) defending the use of (1) formulæ representing hypothetical intermediate products and (2) of "incomplete" formulæ, such as the second in the scheme $OH\cdot CArR\cdot CHIR' \longrightarrow OH\cdot C\overset{|}{Ar}R\cdot \overset{\downarrow}{C}R' \longrightarrow OH\cdot CR\colon CArR'$, on the ground of their convenience in illustrating the mechanism of complex reactions. T. A. H.

Action of the Silent Electric Discharge on Moist Methane. Walther Löb (*Ber.*, 1908, 41, 87—90).—By the action of the silent discharge on moist methane, a colourless solid is formed, insoluble in all solvents, along with small quantities of the methyl esters of higher aliphatic acids. The solid is a polymeride of $C_9H_{15}O$, and agrees with the solid obtained from acetylene by Losanitsch (this vol., ii, 32). Analysis of the gases formed during the experiment shows that in the first place hydrogen is eliminated and unsaturated hydrocarbons are formed, which condense with water to form the insoluble compound. E. F. A.

Preparation of Ethylenic Hydrocarbons. Transformation of Primary Alcohols into Aldehydes and Hydrogen. Louis Bouveault (*Bull. Soc. chim.*, 1908, [iv], 3, 117—119, 119—124).—The results recorded in both these papers were obtained in the course of an attempt to simplify and extend the range of applicability of Sabatier and Senderens' method (Abstr., 1903, i, 393) of converting alcohols into aldehydes by the catalytic action of metals. In the first paper, it is pointed out that Ipatieff's results (Abstr., 1903, i, 453, 593, 594, 595, 598) explain the fact observed by the author that, when metallic copper deposited on pumice-stone or on baked clay is employed as a catalyst in Sabatier and Senderens' process, more or less of the corresponding ethylenic hydrocarbon is always formed in addition to the aldehyde; this anomalous result being due to the catalytic action of the pumice and clay respectively. An apparatus suitable for use in applying Sabatier and Senderens' process to complex alcohols is described and figured in the second paper. It consists essentially of a glass or insulated copper tube, heated by a spiral of nickel ribbon conveying an electric current, and containing short rolls of fine copper gauze with finely-divided copper deposited on them by a special process, described in the original. The lower end of the tube is connected to a flask in which the alcohol vapours are generated, and the upper end communicates with a condenser leading to a receiver for the collection of the aldehyde (or ketone) formed. For the lower alcohols, the copper rolls are heated to 300°, but, for the more complex ones, better results are obtained by working under reduced pressure with the copper rolls heated to 250°. Among the products which have been prepared in this way are decaldehyde, phenylacetaldehyde, ethyl *iso*valerylacetate (from ethyl β-hydroxy-β-*iso*butylpropionate), and citral (from geraniol). In the case of unsaturated alcohols, the hydrogen simultaneously formed tends to saturate the ethylenic linking and give rise to the corresponding saturated aldehyde; thus undecylenyl alcohol is converted wholly by this process into undecaldehyde (which furnishes an *oxime*, m. p. 61°, crystallising in spangles). T. A. H.

Mysterious Lack of Carbon in the Condensation Products of Ethylene and Acetylene. MILORAD Z. JOVITSCHITSCH (*Monatsh.*, 1908, **29**, 1—4).—A supposed case of transformation of carbon or hydrogen into another element. The product obtained from ethylene in the author's "synthetisor" (following abstract) contains 13·13% to 13·82% of hydrogen and 79·84% to 80·44% of carbon, whilst the condensation product from acetylene contains 6·87% to 6·98% of hydrogen and 71·23% to 71·96% of carbon. The apparent loss of about 6% in the first, and of about 22% in the second, case is ascribed to the presence in the condensation products of a third element formed under the influence of the dark electric discharge. Both the products are strongly radioactive; especially is this the case with the product from acetylene.

The influence of the Tesla discharge on chemical reaction is of the same nature as that of the electric spark. G. Y.

Condensation Products Obtained from Ethylene and Acetylene by Means of the Dark Electric Discharge. MILORAD Z. JOVITSCHITSCH (*Monatsh.*, 1908, **29**, 5—14. Compare Losanitsch and Jovitschitsch, Abstr., 1897, i, 179; Berthelot, Abstr., 1898, i, 393).—The author has subjected ethylene and acetylene to the action of a current of 3 amperes and 100 volts in the apparatus previously described and now termed a "synthetisor."

The *product* obtained from ethylene is shown to have most probably the formula $C_{30}H_{54}$, and to be a cyclic condensation product. It is oxidised by bromine in ethereal solution, forming a brown, sticky *product*, which when heated with silver nitrate and nitric acid at 100° yields the *silver* salt of a nitro-derivative. When treated with nitric acid at 50—60°, the condensation product yields two *nitro*-derivatives, one of which, $C_7H_{11}O_2N$, is soluble, whilst the other, $C_6H_9O_2N$, is insoluble, in hot alcohol.

The condensation *product* from acetylene has probably the formula $C_{30}H_{26}$, and forms a *dibromide*, $C_{30}H_{26}Br_2$, with bromine at the ordinary temperature, or in ethereal solution at 100° a mixture of this with a *bromo-dibromide*, $C_{30}H_{25}Br_3$; with an excess of bromine at 100° in absence of a solvent, a *dibromo-dibromide*, $C_{30}H_{24}Br_4$, is formed. The condensation product reacts with fuming nitric acid, forming a *product*, $C_{30}H_{25}O_{30}N_3$. G. Y.

Colour of Ethylene Glycol and of Glycerol. WALTHÈRE SPRING (*Arch. Sci. phys. nat.*, 1908, [iv], **25**, 5—14; *Bull. Soc. chim. Belg.*, 1908, **22**, 10—17).—In order to obtain evidence of the part played by the hydroxyl group in the blue colour which water and ethyl alcohol exhibit when examined in long columns, the author has investigated the colour of pure ethylene glycol and glycerol. Ethylene glycol, purified by distillation at low pressures, has a yellow colour which is shown to be due to traces of impurities. Attempts were made to remove the yellow colour by treatment with freshly-calcined animal charcoal, but it was found that the filtered liquid was almost opaque in consequence of the presence of ultra-microscopic particles of charcoal which could not be removed by filtration. When, however, the glycol was mixed with one-fifth of its volume of water, filtration after treatment with charcoal gave an optically clear liquid. A similar phenomenon was observed in the attempts to remove the green colour which glycerol shows after purification by distillation in steam under reduced pressure.

Ethylene glycol and glycerol, mixed with one-fifth volume of water and treated with animal charcoal as described, exhibit a blue colour, which is deeper than the blue colour of ethyl alcohol and water, when columns of the substances corresponding with equimolecular quantities are compared. The observations indicate that the hydroxyl group is the determining factor in the production of this colour.

H. M. D.

Alkylene Glycol-chlorohydrin Ethers and their Transformations. Paul Hoering (*Ber.*, 1908, 41, 173—175).—Attention is drawn by the author to his investigations (Abstr., 1905, i, 903; 1907, i, 624) and those of Hell and Hollenburg (Abstr., 1896, i, 354) dealing with several of the points discussed in Houben and Fuhrer's paper (this vol., i, 73) of which these authors make no mention.

W. H. G.

Preparation of Esters. Albert Reychler (*Bull. Soc. chim. Belg.*, 1907, 21, 428—434).—Krafft and Roos have shown (Abstr., 1894, i, 91) that the sulphonic acids facilitate the formation of ethers and esters, and the Badische Anilin- und Soda-Fabrik has patented a process for the use of sulphonic acids in accelerating the action of acetic anhydride on cellulose (*Chem. Zentr.*, 1907, ii, 365). The author finds that camphorsulphonic acid greatly accelerates the action of acid anhydrides on phenols and alcohols, and has prepared in this way acetyl derivatives of geraniol, glycerol, phenol, quinol, gallic acid, salicylic acid, and methyl salicylate. Butyrates of the first and second, and benzoates of the first, third, and seventh, substances were also prepared. In most cases, simple addition of a small quantity of camphorsulphonic acid to the cold mixture of alcohol or phenol with the anhydride only is required, but in others the mixture must be heated.

T. A. H.

Oxidation of Ammonium Salts of Saturated Fatty Acids with Hydrogen Peroxide. Henry D. Dakin (*J. Biol. Chem.*, 1908, 4, 227—233).—The ammonium salts of the acids from formic to stearic are oxidisable by hydrogen peroxide even at room temperature.

In all cases, carbon dioxide is liberated. Formic acid is most readily oxidised, then follow in order acetic, butyric, and *iso*butyric, and then valeric and *iso*valeric acids. The remaining acids show but slight variations among themselves, yielding about 1/10 gram-mol. of carbon dioxide for every gram-mol. of fatty acid. Propionic acid yields acetaldehyde, acetic acid, and a little formic acid. *iso*Butyric and *iso*valeric acids both yield acetone. The higher acids from hexoic to stearic are oxidised, in part, with formation of ketones derived from β-ketonic acids, as shown thus: $C_nH_{2n+1}CH_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow$

$$C_nH_{2n+1}CO{\cdot}CH_2{\cdot}CO_2H \longrightarrow C_nH_{2n+1}CO{\cdot}CH_3 + CO_2.$$

Lower fatty acids and aldehydes are formed simultaneously. The reactions appear to have some biochemical relationships, which will be investigated further. W. D. H.

Catalytic Ester Exchanges. II. ROBERT KREMANN (*Monatsh.*, 1908, **29**, 23—44. Compare Abstr., 1905, ii, 630).—According to the view of the mechanism of the formation of ethyl acetate and glycerol from triacetin and ethyl alcohol put forward previously, the amount of triacetin in the equilibrium mixture must increase as the amount of alcohol is diminished; moreover, triacetin, or a mixture of this with mono- and di-acetin, must be formed by the action of glycerol on ethyl acetate, the reaction being accelerated by addition of sodium hydroxide. These requirements are shown to be satisfied by the experimental results obtained. Stritar and Fanto's criticisms (Abstr., 1907, i, 464) are founded on a misapprehension of the present author's views. If hydrolysis does take place, both the triacetin and the ethyl acetate must undergo the reaction, but in absolute alcoholic solution the amount of hydrolysis is negligible. In aqueous alcohol, on the other hand, the velocity of the hydrolysis increases rapidly with the percentage of water.

The amounts of ethyl acetate formed by diacetyltartaric acid and its ethyl ester in varying concentrations of alcoholic sodium hydroxide have been determined. The yields of ethyl acetate from the diacetyl acid with the higher concentrations of the alkali are approximately the same as those obtained from tetra-acetylmucic acid, but diminish less rapidly with diminishing concentration of the alkali. Ethyl diacetyltartrate yields less ethyl acetate than does the acid with the higher, but more with the lower, concentrations of the alkali. It is remarkable that the ester exchange takes place with diacetyltartaric acid on addition of less alkali than is required for the neutralisation of the acid. G. Y.

Constitution of Glucinum Salts of Fatty Acids. New Glucinum Ortho-Salts and Salts of Other Elements with Organic Ortho-Acids. BORIS GLASSMANN [and, in part, A. NOVICKY] (*Ber.*, 1908, **41**, 33—38. Compare Abstr., 1907, i, 109).—Salts of the type Gl_2R_2O (R = acid radicle) are obtained by the action of glucinum carbonate on hydroxy-acids and halogen-substituted fatty acids; it is assumed that these salts are derived from acids formed by the condensation of 2 mols. of an ortho-fatty acid. The author further shows that a large number of well-known salts of other metals may be regarded as salts of ortho-fatty acids, or acids formed by the condensation of 2 or more mols. of these acids; for example, basic glucinum acetate, $Gl_4O(OAc)_6$ (Steinmetz, Abstr., 1907, i, 673); zirconyl acetate, $ZrO(OAc)_2$ (Rosenheim and Hertzmann, Abstr., 1907, ii, 271), and basic chromium propionate, $Cr_2O(Et\cdot CO_2)_4$ (Renard, Abstr., 1887, 654).

The following crystalline salts of glucinum were prepared and analysed: *lactate*, $Gl_2O(C_3H_5O_3)_2,H_2O$; *glycollate*, $Gl_2O(C_2H_3O_3)_2,H_2O$; *ethylglycollate*, $Gl_2O(C_4H_7O_3)_2,H_2O$; *phenylglycollate*, $Gl_2O(C_8H_7O_3)_2$; *salicylate*, $Gl_2O(C_7H_5O_3)_2$, and *a-chloropropionate*, $Gl_2O(C_3H_4O_2Cl)_2,H_2O$; the *trichloroacetate*, $Gl_2O(C_2O_2Cl_3)_2$, is obtained as a glassy mass. The following crystalline glucinum salts of the type Gl_4R_6O, corresponding with the above-mentioned basic acetate, have also been obtained: *dichloroacetate*, $Gl_4O(C_2HO_2Cl_2)_6$; *bromoacetate*, $Gl_4O(C_2H_2O_2Br)_6$; *chloroacetate*, $Gl_4O(C_2H_2O_2Cl)_6$, and *a-bromopropionate*, $Gl_4O(C_3H_4O_2Br)_6$; the *cyanoacetate*, $Gl_4O(C_3H_2O_2N)_6$, is obtained as a vitreous mass. The solution obtained by dissolving freshly precipitated stannous oxide in strong acetic acid yields on evaporation the crystalline *stannoacetate*, $Sn(OAc)_2O$. W. H. G.

Some Cuprammonium Salts. V. David W. Horn (*Amer. Chem. J.*, 1908, **39**, 184—226. Compare Abstr., 1906, ii, 231; 1907, i, 595; ii, 871).—Experiments are described which have been carried out with the object of ascertaining whether the largest number of ammonia groups which can combine with copper salts is a function of the basicity of the acid residue.

The method adopted was that described previously (Abstr., 1907, ii, 532) for determining transition temperatures. The anhydrous copper salt is treated with liquid ammonia, a constant pressure of about one atmosphere is maintained, and by observing the thermometer it can be ascertained whether the same solid compound existing at the temperature at which the saturated solution boils persists until the whole system has attained the temperature of the room, or whether it decomposes to form a simpler compound at intermediate temperatures.

It has been found that at all pressures not greater than one atmosphere, and at all temperatures between $-30°$ and $+20°$, copper sulphate, oxalate, and succinate cannot combine with more than five ammonia groups, whilst the chloride, bromide, and iodide are capable of uniting with six ammonia groups. Copper acetate forms a salt containing $4NH_3$, and evidence was obtained of the existence of a salt containing still more ammonia, and having a tension of one atmosphere when it dissociates at about $-22°$; its formula was not established.

Copper thiocyanate yields, in addition to the salts already described (Abstr., 1907, i, 596), a *compound*, $Cu(SCN)_2,5NH_3$. When the salt, $Cu(SCN)_2,2NH_3$, is treated with pyridine, a *compound*, probably $Cu(SCN)_2,4C_5H_5N$, is produced.

When copper acetoiodide is treated with liquid ammonia, a mixture of the acetate, $Cu(C_2H_3O_2)_2,4NH_3$, and the iodide, $CuI_2,6NH_3$, appears to be formed. The acetobromide behaves in the same manner.

Copper dithionate does not form a compound containing more ammonia than the salt, $2CuS_2O_6,9NH_3$, at any temperature between −30° and +20°. Copper *o*-phthalate yields a *salt*, $2CuC_8H_4O_4,9NH_3$, and indications were obtained of the existence of a still higher salt with a tension of one atmosphere when dissociating at about −8°. In the case of copper carbonate, a salt containing more than $2NH_3$ could not be obtained. Copper nitrate yields a *salt*,

$$4Cu(NO_3)_2,23NH_3.$$

A list of copper salts is given, arranged in the order of their solubility in liquid ammonia.

The colour of the cuprammonium compounds depends not only on the number of ammonia groups in the molecule, but also on the acid residues.

The order of the copper salts with regard to their affinity for ammonia is as follows: copper iodide, bromide, chloride, nitrate, sulphate, succinate, oxalate, thiocyanate, dithionate, acetate. The iodide, bromide, and chloride, containing $6NH_3$, dissociate under 2 cm. pressure at 67·4°, 54·9°, and 46·7° respectively. The sulphate, succinate, and oxalate, with $5NH_3$, when left over sulphuric acid at the ordinary temperature, lose $1NH_3$, in one week, one day, and one and a-half hours respectively. The thiocyanate, $Cu(SCN)_2,5NH_3$, is less stable, as, under atmospheric pressure, it dissociates at about 10°, whilst all these other salts containing $5NH_3$ dissociate at about 20°.

The nature of the affinity of copper salts for ammonia is discussed.

E. G.

Electrolytic Production of Saturated Acids and Esters from the corresponding Unsaturated Compounds. C. F. Boehringer and Söhne (D.R.-P. 187788).—The unsaturated acids and their esters are readily reduced in the cathode cell to the corresponding saturated compounds, providing that a cathode of platinised platinum is employed. Cathodes of nickel or polished platinum are useless, owing to the small yield thereby obtained. The hydrogenation takes place in acid solutions, small current densities being employed. The unsaturated acid or its ester may be either in suspension or dissolved in a suitable solvent, such as alcohol.

Oleic acid is converted into stearic acid in alcoholic solution containing a small amount of sulphuric acid at 20—50°, the current density being 1 ampere per sq. metre with 4 to 6 volts.

Ethyl oleate and erucic acid are similarly reduced to ethyl stearate and behenic acid respectively. G. T. M.

Magnesium, Calcium, and Strontium Salts of the Higher Brominated Fatty Acids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 187449).—An alcoholic solution of calcium chloride was saturated with ammonia, filtered from precipitated ammonium chloride, and treated with an alcoholic solution of bromobehenic acid. *Calcium bromobehenate*, $Ca(C_{22}H_{42}BrO_2)_2$, thus produced is a colourless, tasteless powder, insoluble in water or alcohol; it may also be prepared either by the direct treatment of the acid with saturated lime-water or by double decomposition from soluble calcium salts and the alkali bromobehenates in aqueous solution.

Strontium bromobehenate, $Sr(C_{22}H_{42}BrO_2)_2$, prepared by the interaction of strontium hydroxide and bromobehenic acid in methyl-alcoholic solution, resembles the preceding salt; the corresponding *magnesium* salt has similar properties, and is produced by comparable processes.
G. T. M.

The Addition of Hydrogen Iodide to the Unsaturated Fatty Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 187822).—It has been found that hydrogen iodide may be readily added to the unsaturated fatty acids by treating these with a metallic iodide and some stronger acid in the absence of water.

Erucic acid is converted into iodobehenic acid when shaken for two or three days at 40—50° with sodium iodide and glacial acetic acid saturated with hydrogen chloride.

Oleic acid is transformed into iodostearic acid by treatment at 70—80° with potassium iodide and oxalic acid suspended in benzene. Other metallic iodides may be employed instead of potassium iodide, and sulphuric, phosphoric, tartaric, or benzenesulphonic acid may be used as the condensing agent. G. T. M.

Psylla Wax. IV. Psyllic Acid and its Salts. ERNST E. SUNDVIK (*Zeitsch. physiol. Chem.*, 1908, **54**, 255—257. Compare Abstr., 1898, i, 617; 1901, i, 358; 1907, i, 887).—The alkali salts of psyllic acid (pysslostearic acid) are precipitated when alcoholic solutions of the acid and an alkali hydroxide are mixed. The *silver* and *barium* salts can be obtained by adding aqueous alcoholic solutions of silver nitrate and barium chloride to alcoholic solutions of the acid. The following salts have been analysed: $C_{33}H_{65}O_2Na$, $C_{60}H_{130}O_4Ba$, and $C_{33}H_{65}O_2Ag$. Psylla wax is hydrolysed by alcoholic potassium hydroxide as well as by hydrobromic acid. J. J. S.

Alcoholysis of Linseed Oil. ALBIN HALLER (*Compt. rend.*, 1908, **146**, 259—262. Compare Abstr., 1907, i, 9, 10, 379).—Four specimens of linseed oil having respectively the iodine numbers 176, 168, 171, and 172, and the saponification values 185, 190, 189, and 191, have been examined. The oil being insoluble in methyl and ethyl alcohols, addition of a second solvent was necessary; benzene, carbon tetrachloride, acetone, and ether were tried, of which the last was found most suitable. When linseed oil is boiled with a mixture of ethyl ether and methyl alcohol containing 2·5% of hydrogen chloride, methyl palmitate, arachate, stearate, oleate, linoleate, linolenate, and *iso*linolenate are formed. The glycerides of stearic acid, which occurs in appreciable proportions, and of arachic acid, which occurs only in very small quantities, have not prevously been recognised in linseed oil.
E. H.

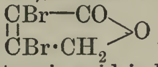
Transformation of the α-Hydroxy-acids into Aldehydes by Boiling the Aqueous Solutions of their Mercuric Salts. Application to the Preparation of *l*-Arabinose by Means of Mercuric Gluconate. MARCEL GUERBET (*Compt. rend.*, 1908, **146**, 132—135).—According to the equation $2Hg(C_3H_5O_3)_2 = C_3H_6O_3 + Hg_2(C_3H_5O_3)_2 + C_2H_4O + CO_2$, proposed by the author (Abstr., 1902, i, 703) to explain the decomposition of an aqueous solution of mercuric lactate when boiled, 100 grams of this salt should give 57·8 grams of mercurous lactate, 9 grams of lactic acid, and 4·4 grams of acetaldehyde. In a quantitative experiment, the amounts obtained were 55·4 grams, 11·4 grams, and 3·9 grams respectively, and the conclusion is drawn that the chief reaction is represented by the above equation, the differences between the theoretical and experimental numbers probably being due to the gradual decomposition of the mercurous lactate into mercuric lactate and mercury. Mercuric glycollate and tartrate similarly decompose into the mercurous salts, the acids, carbon dioxide, and formaldehyde and glyoxal respectively, but here the reactions are slower than with the lactate. Mercuric gluconate undergoes the same reaction, and, as in this case the secondary change of the mercurous salt formed into mercuric gluconate and mercury is much more rapid than the corresponding change in the former reactions, two instead of one of the four molecules of gluconic acid present as mercuric salt are transformed into *l*-arabinose. The latter can be prepared advantageously by this reaction, a total yield of 22—24 grams being obtainable from 100 grams of calcium gluconate. E. H.

Mechanism of the Acetoacetic Ester Synthesis. I. The Condensation of Acetone with Oxalic Ester. Robert H. Clark (*J. Physical Chem.*, 1908, 12, 1—25).—The author has measured the velocity of formation of ethyl acetonyloxalate in alcohol with various concentrations of acetone, ethyl oxalate, and sodium ethoxide (catalyst), and also the effect of water and of alcohol on the yield (compare Claisen and Stylos, Abstr., 1887, 917). It was found that the degree of coloration produced by excess of ferric chloride in neutral solution is proportional to the amount of ethyl acetonyloxalate present, and is not affected by water, alcohol, acetone, or ethyl oxalate; an equivalent of sodium ethoxide, however, doubles the intensity of the red colour produced. The author supposes that the sodium ethoxide gives rise to a new enol group (compare Schiff, Abstr., 1898, i, 355), and argues that ethyl acetonyloxalate should be formulated as

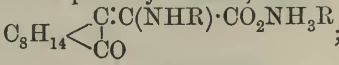
$$COMe{\cdot}CH{:}C(OH){\cdot}CO_2Et,$$

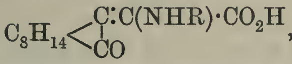
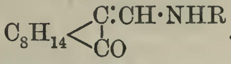
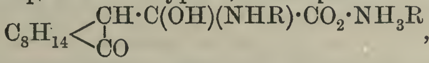
or $OH{\cdot}CMe{:}CH{\cdot}CO{\cdot}CO_2Et$, neither of which formulæ agrees with the magnetic rotation and refractive index of the substance as determined by Perkin and Gladstone (Trans., 1892, 61, 821).

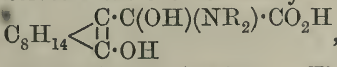
Experiments made with a colorimeter showed that in strong, absolute alcoholic solutions the condensation is complete, but the yield is diminished somewhat by dilution with alcohol. Traces of water, however, have a very marked effect, the addition of only 1·065% of water lowering the yield from 96% to 10% of the theoretical. The condensation is shown to be a reversible reaction. In alcoholic solutions, the rate of condensation is proportional to the first power of the acetone condensation, and to a power of the concentration of ethyl oxalate and sodium ethoxide, which varies from 1·2 to 2 with increasing dilution. The author claims that his results lend support to Claisen's theory that the change is preceded by the association of sodium ethoxide with the ester, the degree of association depending on the concentration of the solutions. The additive product must have twice the molecular weight assumed by Claisen and Lowman (Abstr., 1887, 583). R. J. C.

γ-Hydroxytetrolic Acid. ROBERT LESPIEAU and VIGUIER (*Compt. rend.*, 1908, **146**, 294—296).—The authors have applied Jocitsch's reaction of organo-magnesium compounds on acetylenic hydrocarbons to propargyl alcohol. The latter (1 mol.) when treated with magnesium ethyl bromide (2 mols.) gives *γ-hydroxytetrolic acid*, $OH\cdot CH_2\cdot C⋮C\cdot CO_2H$, a white, crystalline substance, m. p. 115—116°, which decomposes carbonates, but, unlike Duisberg's hydroxytetrolic acid (Abstr., 1882, 1193), does not give a sky-blue coloration with ferric chloride. When treated in the dark in ethereal solution at $-10°$ with bromine (1 mol.), it is converted into a mixture of much *αβ-dibromo-γ-hydroxy-Δ^{α}-butenoic acid*, $OH\cdot CH_2\cdot CBr:CBr\cdot CO_2H$, m. p. 137—138°, with a small quantity of Tönnies's lactone (Abstr., 1879, 918), which Hill (Abstr., 1894, i, 319) has shown to have the formula  $\begin{array}{l}CBr—CO\\ CBr\cdot CH_2\end{array}\!\!>O$; it has m. p. 91°.

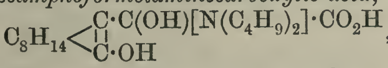
When αβ-dibromo-γ-hydroxy-Δ^{α}-butenoic acid is kept at 150° for two hours, its m. p. remains unchanged; when heated at 200°, it loses carbon dioxide and hydrogen bromide, but no lactone is formed. This seems to indicate that the acid belongs to the fumaric rather than to the maleic series. E. H.

Camphoroxalic Acid Derivatives. XI. Action of Certain Secondary Amines on Camphoroxalic Acid. J. BISHOP TINGLE and L. F. WILLIAMS (*Amer. Chem. J.*, 1908, **39**, 105—124. Compare Abstr., 1899, i, 444; 1900, i, 302; 1901, i, 632; 1905, i, 799; 1906, i, 902).—In earlier papers, compounds of camphoroxalic acid with amines have been described. In the case of primary amines, derivatives are produced of the types: (I)  $C_8H_{14}<\begin{array}{l}C:C(NHR)\cdot CO_2NH_3R\\ CO\end{array}$;

(II)  $C_8H_{14}<\begin{array}{l}C:C(NHR)\cdot CO_2H\\ CO\end{array}$, and (III)  $C_8H_{14}<\begin{array}{l}C:CH\cdot NHR\\ CO\end{array}$. In the formation of compounds of type I, it is probable that intermediate products,  $C_8H_{14}<\begin{array}{l}CH\cdot C(OH)(NHR)\cdot CO_2\cdot NH_3R\\ CO\end{array}$, are first formed, water being afterwards eliminated. Some of these intermediate compounds are stable, and have been described under the name of camphoformolamine derivatives.

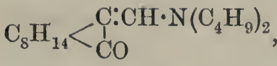
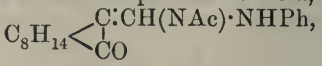
The compounds derived from the secondary amines probably have the constitution  $C_8H_{14}<\begin{array}{l}C\cdot C(OH)(NR_2)\cdot CO_2H\\ C\cdot OH\end{array}$, and are therefore termed *iso*camphoformolamine derivatives. They give an intense violet coloration with ferric chloride.

Diisobutylaminecamphoformolaminecarboxylic acid,



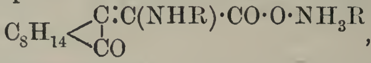
$$C_8H_{14}<\begin{array}{l}C\cdot C(OH)[N(C_4H_9)_2]\cdot CO_2H\\ C\cdot OH\end{array},$$

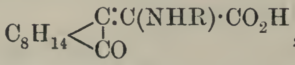
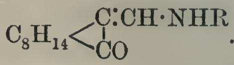
m. p. 179—180° (decomp.), forms white needles, and when heated above its m. p. is converted into *diisobutylcamphoformeneamine*,

 $C_8H_{14}<\begin{array}{l}C{:}CH\cdot N(C_4H_9)_2\\ |\\ CO\end{array}$, m. p. 73—74°. The following compounds are also described: *diamyl*iso*camphoformolaminecarboxylic acid*, m. p. 160°; *diamylcamphoformeneamine*, m. p. 43°; *diï*so*amyl*iso*camphoformolaminecarboxylic acid*, m. p. 156°; *diï*so*amylcamphoformeneamine*, m. p. 40°; *dibenzylcamphoformeneamine*, m. p. 152°; *phenylmethylcamphoformeneamine*, m. p. 126°; *phenylethylcamphoformeneamine*, b. p. 285°/110 mm.; *benzylethyl*iso*camphoformolaminecarboxylic acid*, m. p. 158° (decomp.), and *benzylethylcamphoformeneamine*, m. p. 57°. By the action of acetylphenylhydrazine on camphoroxalic acid, *acetylphenylaminecamphoformeneamine*,  $C_8H_{14}<\begin{array}{l}C{:}CH(NAc)\cdot NHPh\\ |\\ CO\end{array}$, m. p. 174°, is obtained.

Benzoylphenylhydrazine, benzylphenylhydrazine, benzylmethylamine, phenylmethylhydrazine, benzylaniline, phenyl-β-naphthylamine, p-phenylhydrazinesulphonic acid, and various acyl derivatives of o- and p-aminophenols were heated with camphoroxalic acid, but condensation products were not formed.

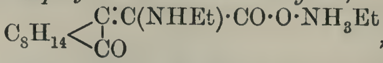
Dimroth's paper (Abstr., 1907, i, 662) on the interaction of p-nitrobenzenediazonium hydroxide and certain ketonic and enolic compounds is criticised. E. G.

Camphoroxalic Acid. XII. Action of Primary and Tertiary Amines on Camphoroxalic Acid. J. Bishop Tingle and L. F. Williams (*Amer. Chem. J.*, 1908, **39**, 277—300. Compare preceding abstract).—In earlier papers, it has been shown that primary amines condense with camphoroxalic acid with formation of substances of three types: (I)  $C_8H_{14}<\begin{array}{l}C{:}C(NHR)\cdot CO\cdot O\cdot NH_3R\\ |\\ CO\end{array}$,

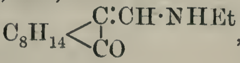
(II)  $C_8H_{14}<\begin{array}{l}C{:}C(NHR)\cdot CO_2H\\ |\\ CO\end{array}$, and (III)  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NHR\\ |\\ CO\end{array}$.

It is pointed out that, whilst certain amines yield compounds of all three types, others give only two, and some not more than one of them; in the last case, substances of type III being usually formed. Moreover, many amines do not react at all with camphoroxalic acid. In order to obtain evidence as to the causes underlying these differences in behaviour, the investigation has been extended to primary amines not previously examined. A study has also been made of the behaviour of certain tertiary bases towards camphoroxalic acid, particularly in the hope of obtaining well-crystallised salts which might possibly be of use in the resolution of the acid into structural isomerides.

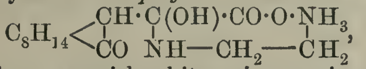
Ethylamine ethylcamphoformeneaminecarboxylate,



$$C_8H_{14}<\begin{array}{l}C{:}C(NHEt)\cdot CO\cdot O\cdot NH_3Et\\ |\\ CO\end{array},$$

m. p. 109°, forms white needles, and, when heated at 150°, is converted into *ethylcamphoformeneamine*,  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NHEt\\ |\\ CO\end{array}$, m. p. 118°.

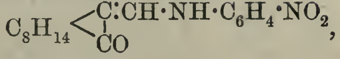
Ethylenediamine yields a *camphoformolamine* derivative,



$$C_8H_{14}<\begin{array}{l}CH\cdot C(OH)\cdot CO\cdot O\cdot NH_3\\ CO\quad NH-CH_2-CH_2\end{array},$$

m. p. 220°, which forms greyish-white, microscopic crystals.

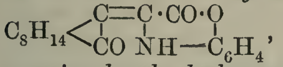
p-*Nitrophenylcamphoformeneamine*,



$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot NH\cdot C_6H_4\cdot NO_2\\ CO\end{array},$$

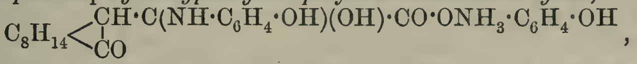
m. p. 156°, forms lustrous, brownish-yellow needles.

o-Aminophenol reacts with camphoroxalic acid with formation of the *lactone* of *o-hydroxyphenylcamphoformeneaminecarboxylic acid*,



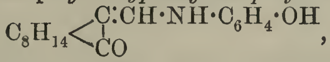
$$C_8H_{14}<\begin{array}{l}C=C\cdot CO\cdot O\\ CO\quad NH-C_6H_4\end{array},$$

m. p. 159·5°, whilst *p*-aminophenol yields p-*aminophenol* p-*hydroxyphenylcamphoformolaminecarboxylate*,



$$C_8H_{14}<\begin{array}{l}CH\cdot C(NH\cdot C_6H_4\cdot OH)(OH)\cdot CO\cdot ONH_3\cdot C_6H_4\cdot OH\\ CO\end{array},$$

m. p. 190°, which is converted by dilute hydrochloric acid into the corresponding *acid*, m. p. 178° (decomp.). When this acid is heated above its m. p., it gives p-*hydroxyphenylcamphoformeneamine*,



$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot NH\cdot C_6H_4\cdot OH\\ CO\end{array},$$

m. p. 314°.

n-Propylamine and *m*- and *p*-phenylenediamines appear to react with camphoroxalic acid, but definite products could not be isolated.

The *camphoroxalates* of trimethylamine, m. p. 139—140° (decomp.), triethylamine, m. p. 102—103°, quinine, m. p. 160—161° (decomp.), strychnine, m. p. 214—215° (decomp.), and brucine, m. p. 235—236° (decomp.), are described. A crystalline camphoroxalate of tribenzylamine could not be obtained. Attempts to prepare two isomeric brucine camphoroxalates were unsuccessful.

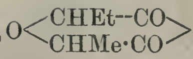
Benzylideneaniline reacts with camphoroxalic acid with formation of phenylcamphoformeneaminecarboxylic acid, which was first obtained (Abstr., 1899, i, 444) by the action of aniline on camphoroxalic acid. The production of this compound is attributed to the hydrolysis of the benzylideneaniline into aniline and benzaldehyde.

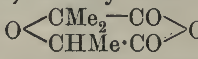
Piperine does not react with camphoroxalic acid.

Tetraethylammonium camphoroxalate forms white needles, and is very unstable.

A list is appended of the various amines studied in this connexion, together with the formulæ and m. p.'s of the products obtained.

E. G.

New Homologues of Diglycollic Acid. ÉMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1908, **146**, 26—29. Compare Abstr., 1907, i, 748).—When ethyl α-bromobutyrate acts on the sodium compound of ethyl lactate, there is formed *ethyl α-methyl-α′-ethyldiglycollate*, $CO_2Et\cdot CHMe\cdot O\cdot CHEt\cdot CO_2Et$, a liquid with an ethereal odour, having b. p. 130°/25 mm., D^{16} 1·0774. The free *acid*, which crystallises in small needles, m. p. 69°, loses water, partly on distillation in a vacuum and completely when boiled with acetyl chloride, giving the *anhydride*,  $\mathrm{O}<\begin{matrix}\mathrm{CHEt{-}CO}\\ \mathrm{CHMe\cdot CO}\end{matrix}>\mathrm{O}$, a mobile liquid with a piquant odour, b. p. 125—130°/20 mm., D^{16} 1·1556.

By the action of alcoholic ammonia on the ethyl ester, the *diamide*, $NH_2\cdot CO\cdot CHMe\cdot O\cdot CHEt\cdot CO\cdot NH_2$, is formed in fine needles, m. p. 140—142°. A similar reaction with ethyl α-bromo*iso*butyrate gives *ethyl αα-dimethyl-α′-methyldiglycollate*, $CO_2Et\cdot CMe_2\cdot O\cdot CHMe\cdot CO_2Et$, a mobile liquid, b. p. 130—135°/25 mm., D^{16} 1·0507. The *acid*, which has not been obtained crystalline, is dehydrated by boiling acetyl chloride, giving the *anhydride*,  $\mathrm{O}<\begin{matrix}\mathrm{CMe_2{-}CO}\\ \mathrm{CHMe\cdot CO}\end{matrix}>\mathrm{O}$, a liquid, b. p. 112—116°/20 mm., D^{16} 1·1531. The *diamide*, prepared from the ester, forms colourless lamellæ, m. p. 150° (after softening). *Ethyl α′-methyl-α-*iso*propyldiglycollate*, $CO_2Et\cdot CHMe\cdot O\cdot CHPr^{\beta}\cdot CO_2Et$, is similarly prepared. It is a colourless liquid, b. p. 137—140°/15 mm , D^{16} 1·0398. In the last reaction, the yield is very poor. By means of their brucine salts, the authors have separated αα′-dimethyldiglycollic acid, $O(CHMe\cdot CO_2H)_2$, into its two optically active modifications.

E. H.

Electrolysis of Sugars. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 7, 527—528).—*d*-Gluconic acid has been electrolysed in the hope of synthesising a polyhydric alcohol containing 10 carbon atoms. In reality, decomposition occurred, and *d*-arabinose was obtained. Other polyhydroxy-acids behave in a similar manner: *l*-arabonic acid yields *l*-erythrose; *i*-erythronic acid, *i*-glyceraldehyde; *i*-glyceric acid, glycollaldehyde, and glycollic acid, formaldehyde. In each case, the reaction consists in the elimination of a molecule of formic acid from one of the hydroxy-acid. In a few instances, indications were obtained of the formation of ketonic acids of the type

$$OH\cdot CH_2\cdot[CH\cdot OH]_x\cdot CO\cdot CO_2H.$$

When melibionic acid is subjected to electrolysis, a sugar containing 11 carbon atoms is formed. Saccharic acid, under similar conditions, yields the dialdehyde of tartaric acid, and tartaric acid itself yields glyoxal. Serine and *iso*serine when electrolysed yield products which react with *p*-nitrophenylhydrazine.

J. J. S.

Saccharinic Acids. HEINRICH KILIANI (*Ber.*, 1908, 41, 158—167).—Chiefly polemical against Nef (this vol., i, 5). The work of Kiliani and Loeffler (Abstr., 1904, i, 373; 1905, i, 737) has been repeated on a large scale, and their results confirmed. No new compound was isolated from the product formed by the action of calcium hydroxide on lactose, but a new calcium saccharinate has been obtained by the action of calcium hydroxide on dextrose, the investigation of which is in progress.

W. H. G.

Decomposition of Calcium and Barium Tartrates by Alkali Chlorides. H. CANTONI and MADAME JOLKOWSKY (*Bull. Soc. chim.*, 1907, [iv], 1, 1181—1189. Compare Abstr., 1905, i, 14, 633).—In previous papers, the solubilities of these tartrates in water at various temperatures were given, and attention was directed to the fact that a difficulty was experienced in devising a method for the estimation of tartaric acid by the precipitation of an insoluble tartrate, since the precipitates formed proved to be more soluble in the solution of the second salt, simultaneously produced, than in water. In the present paper, it is shown that calcium tartrate is more soluble than barium tartrate in aqueous solutions of potassium, sodium, or ammonium chloride, and that the action of each of these three chlorides on each of the tartrates increases in the order given, although the differences are not great. In all cases, the solubility increases to about the same extent with rise of temperature. The attack of the tartrates by the chloride solutions is vigorous during the first hour, moderates considerably in the second hour, and equilibrium is reached at the end of about four hours. The solubility of each of the tartrates increases with increase of concentration of the chloride used, but the increase in the case of barium tartrate is more rapid than in the case of calcium tartrate.

Tables and curves illustrating in detail the results obtained are given in the original. T. A. H.

Sodium Antimonyl Tartrate. R. H. ADERS PLIMMER (*Proc. Roy. Soc.*, 1908, *B*, **80**, 11—12).—Sodium antimonyl tartrate has the composition $C_4H_4O_7NaSb,2\frac{1}{2}H_2O$. On drying at 105°, $2H_2O$ are lost, and the remaining $\frac{1}{2}$ mol. is removed by exposure in a vacuum over sulphuric acid. G. B.

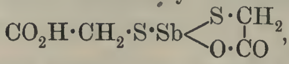
Methyl αγ-Dibromo- and Dichloro-dicarboxyglutarate and the Formation of *cyclo*Trimethylene Derivatives from the Former. MAX GUTHZEIT and MARTIN LOBECK (*J. pr. Chem.*, 1908, [ii], **77**, 43—60).—*Methyl αγ-dibromodicarboxyglutarate* [*methyl αγ-dibromopropanetetracarboxylate*], $CH_2[CBr(CO_2Me)_2]_2$, prepared by the action of bromine on methyl propanetetracarboxylate in carbon disulphide solution at 35°, crystallises in prisms, m. p. 125—126°, and again forms methyl propanetetracarboxylate when boiled with zinc dust in benzene solution. The *dichloro*-ester, prepared by the action of chlorine on methyl propanetetracarboxylate at 50°, crystallises in prisms, m. p. 128—129°. The action of sodium on the dibromo-ester in boiling toluene solution leads to the formation of methyl *cyclo*trimethylenetetracarboxylate, which is formed also when the dibromo-ester is heated with methyl disodiopropanetetracarboxylate or sodium methoxide in methyl-alcoholic solution, or is treated with ammonia in hot methyl-alcoholic solution. *cyclo*Trimethylenetetracarboxylic acid has m. p. 208° (decomp.) (200°, Guthzeit and Dressel, Abstr., 1890, 879 ; 218—220°, Gregory and Perkin, Trans., 1903, **83**, 780). Ethyl dibromopropanetetracarboxylate, under the same conditions, yields ethyl *cyclo*trimethylenetetracarboxylate (Perkin, Trans., 1905, **87**, 358), m. p. 43°.

When saturated with ammonia in cooled methyl-alcoholic solution, methyl dibromopropanetetracarboxylate yields a *product*, crystallising in needles, which on analysis gives figures agreeing approximately with those required by cyclo*trimethylenetetracarboxylamide*; this readily loses ammonia, and on hydrolysis forms carbon dioxide and a mixture of *cis*- and *trans*-*cyclo*trimethylenedicarboxylic acids, m. p. 165°. G. Y.

Antimony and Tin Compounds of Thioglycollic Acids. BROR HOLMBERG (*Zeitsch. anorg. Chem.*, 1908, 56, 385—392).—In aqueous solution, sodium chloroacetate and sodium thiostannate react at the ordinary temperature, according to the equation :

$$2CH_2Cl\cdot CO_2Na + Na_3SbS_4 = S_2(CH_2\cdot CO_2Na)_2 + 2NaCl + NaSbS_2,$$

the sodium dithioglycollate remaining in solution. Sodium chloroacetate and thioarsenate react in an exactly corresponding way. Sodium chloroacetate and thiostannate give sodium chloride, sodium sulphide, and sodium thiodiglycollate, $S(CH_2\cdot CO_2Na)_2$.

Attempts to prepare antimony trithioglycollate were unsuccessful ; by interaction of antimony trichloride and thioglycollic acid, only the *compound*  $CO_2H\cdot CH_2\cdot S\cdot Sb<\begin{matrix}S\cdot CH_2\\ |\\ O\cdot CO\end{matrix}$, described by Klason and Carlson (Abstr., 1906, i, 232), was obtained. Sodium chloroacetate and thioantimonite interact in aqueous solution with formation of sodium metathioantimonite and sodium thiodiglycollate.

Stannic chloride, 1 mol., and thioglycollic acid, 2 mols., react readily in ethereal solution, forming the *compound*

$$(S\cdot CH_2\cdot CO_2H)_2,SnCl_2.$$

This compound occurs in colourless crystals, which are unstable, decomposing with excess of water to form the corresponding dihydroxy-compound, $S_2(CH_2\cdot CO_2H)_2,Sn(OH)_2$. The latter occurs as a crystalline powder, practically insoluble in water, but soluble in hydrochloric acid with partial regeneration of the dichloride, and in sodium hydroxide with formation of the corresponding sodium salt. This salt, of the formula $S_2(CH_2\cdot CO_2Na)_2,Sn(OH)_2,6H_2O$, occurs in large, transparent crystals, which slowly decompose in the air. The dichloride, dissolved in absolute alcohol, readily gives the ester, $S_2(CH_2\cdot CO_2C_2H_5)_2,SnCl_2$, m. p. 157—158°. G. S.

Formaldehyde. ALBERT REYCHLER (*Bull. Soc. chim.*, 1907, [iv], 1, 1189—1195 ; *Bull. Soc. chim. Belg.*, 1908, 22, 17—20. Compare A. Lumière, L. Lumière, and Seyewetz, Abstr., 1905, i, 150).—By adding sodium (0·25 gram) to methyl alcohol (100 grams) and then adding trioxymethylene, sufficient of the latter can be dissolved to furnish a liquid containing the equivalent of 57% of formaldehyde. Such a product distils mainly between 89° and 92°, and can be separated into three fractions, whence it is concluded that it contains hydroxydimethyl ether, $MeO\cdot CH_2\cdot OH$, and products of the type

$$OMe\cdot[CH_2O]_n\cdot CH_2\cdot OH.$$

In this reaction, it is supposed that the polyoxymethylene complexes are first opened, yielding sodium alkyloxides, which then react with methyl alcohol, forming sodium methoxide and products of the type indicated. A similar reaction takes place with ethyl or amyl alcohol, glycerol, or menthol, and, when, as in the case of menthol, sodium cannot be introduced directly, an equivalent quantity of sodium methoxide or ethoxide can be used.

Phenol containing a little sodium phenoxide reacts with trioxymethylene at 75—85°, forming an oily, yellow liquid, which is miscible with water and alcohol, partly soluble in ether, and slightly so in benzene. After a time, it becomes insoluble in alcohol. *p*-Cresol and trioxymethylene react at 80—85°, giving a slightly-coloured homogeneous mass, which, after about ten days, can be separated into 2 : 6-dimethylol-*p*-cresol and *p*-homosaligenin (compare Auwers, Abstr., 1907, i, 612). *o*- and *m*-Cresols also react with trioxymethylene, the former yielding crystalline products slowly. With β-naphthol, dihydroxydinaphthylmethane (compare Auwers, *loc. cit.*) is formed, but α-naphthol yields only a resinous product. T. A. H.

Formaldehyde. II. Solid Polymerides of Formaldehyde. FRIEDRICH AUERBACH and HERMANN BARSCHALL (*Chem. Zentr.*, 1907, ii, 1734—1735; from *Arb. Kais. Gesundh.-Amt.*, 1907, 27, 183—230. Compare Abstr., 1905, i, 859).—In view of the disagreements and obscurities existing in regard to the nature of the solid polymerides of formaldehyde, the authors have examined these with a view to determining in how far they are chemical individuals.

Paraformaldehyde, m. p. about 150—160°, which has a mol. wt. at least three times that of formaldehyde, is prepared by evaporation of pure formaldehyde solutions; it is amorphous and colloidal, contains varying amounts of adsorbed water, and reacts with sodium sulphite solution.

α-Polyoxymethylene, $(CH_2O)_n$, formed by addition of 1 vol. of concentrated sulphuric acid to 10 vols. of aqueous formaldehyde, is indistinctly crystalline, m. p. 163—168° in a sealed tube, and at 189° yields a vapour consisting chiefly of formaldehyde molecules.

β-Polyoxymethylene, prepared by adding 4 vols. of concentrated sulphuric acid to 10 vols. of aqueous formaldehyde, is crystalline, m. p. 163—168° in a sealed tube, vapour density 32 at 184°, increasing slowly with the temperature, and reacts with sodium sulphite solution.

γ-Polyoxymethylene, formed together with the β-polymeride by the action of 4 vols. of sulphuric acid on 10 vols. of formalin, is crystalline, m. p. 163—165° in a sealed tube, does not react with sodium sulphite, and when boiled with water is converted into the δ-polymeride; at 184° and 198°, the vapour has D 40 and 60 respectively, the gas consisting of formaldehyde molecules mixed with polymeric molecules, the proportion of the latter increasing with the pressure, but diminishing as the temperature rises. When heated in the open, these three polyoxymethylenes volatilise without first melting.

δ-Polyoxymethylene is indistinctly crystalline, m. p. 169—170° in a sealed tube, melts when heated in the open, does not react with sodium sulphite, and at 190—240° yields a vapour consisting of polymeric molecules which dissociate only slowly.

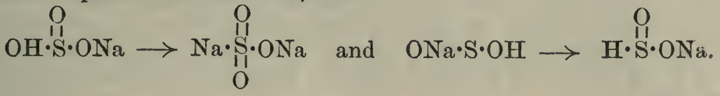
α-Trioxymethylene, $C_3H_6O_3$, formed by sublimation of the polyoxymethylenes into water, crystallises in colourless needles, or strongly refracting prisms, m. p. 63—64° in a sealed tube, b. p. 114·5°/759 mm., volatilises to a marked extent at the ordinary temperature, differs from formaldehyde and the polyoxymethylenes in not giving the aldehyde or ketone reactions, and has therefore probably a cyclic constitution.

Paraformaldehyde differs from α-polyoxymethylene chiefly in being amorphous and in the adsorption of water. Paraformaldehyde and the four polyoxymethylenes yield formaldehyde as gas, or in aqueous solution, with an ease gradually diminishing from paraformaldehyde to δ-polyoxymethylene. The aqueous solutions are not to be distinguished from aqueous formaldehyde.

The conclusions to be drawn from the comparison of the vapour tensions of the four polyoxymethylenes are discussed; the vapour of the polyoxymethylenes at 25° can contain only very little formaldehyde, and must consist chiefly of polymeric molecules insoluble in water. α-Trioxymethylene, on the other hand, has a constant vapour tension and vapour density. G. Y.

So-called Formaldehyde-Sodium Hyposulphite. Ernst von Meyer (*J. pr. Chem.*, 1908, [ii], **77**, 61—64).—In spite of the work of various authors, it has not yet been determined whether sodium formaldehydesulphoxylate (Bazlen, Abstr., 1905, ii, 240) and sodium hydrogen sulphiteformaldehyde, which are formed by the action of sodium hyposulphite on formaldehyde, exist as a double salt or are capable of separate existence in solution in presence of each other. It is now found that the two salts may be separated, at least partly, by fractional precipitation or fractional recrystallisation, and that 1000 mols. of water dissolve 120 mols. of the sulphoxylate and 146 mols. of the sulphite separately, but 93 mols. and 114 mols. respectively, of the two salts in presence of each other. Moreover, a transition point indicating a formation or decomposition of a double salt could not be observed between − 14° and 55° either by the thermometric or the dilatometric method (van't Hoff, Goldschmidt, and Jorissen, Abstr., 1895, ii, 380). Hence sodium hyposulphiteformaldehyde, still sometimes referred to as a chemical individual, consists of a mixture of sodium formaldehydesulphoxylate and sodium hydrogen sulphiteformaldehyde, which do not combine to form a double salt either in the solid state or in solution. G. Y.

Constitution of Sodium Hyposulphite and Formaldehydesulphoxylate. E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1588—1617. Compare Bucherer and Schwalbe, Abstr., 1906, ii, 741).—A criticism of the existing theories as to the constitution of the hyposulphites and formaldehydesulphoxylates is given, and, chiefly on the ground of their reaction with neutral and alkaline solutions of potassium mercuric iodide, it is considered that the former consists of a mixture, $ONa\cdot SO\cdot O\cdot SNa{:}O$ and $ONa\cdot SO\cdot O\cdot SH(OH)\cdot ONa$, together with the free groups $ONa\cdot SH{:}O$ and $OH\cdot SNa{:}O$, the last two being formed when in the preparation of the hyposulphite an insufficient quantity of sodium hydrogen sulphite is employed, but, when sulphur dioxide reacts with metallic sodium, the hyposulphite consists wholly of $SONa\cdot O\cdot SO_2Na$. Sodium formaldehydesulphoxylate is a derivative of hyposulphurous acid, $HS{:}O(OH)$, and should therefore be termed sodium formaldehydehyposulphite. In aqueous solutions, it reacts with other substances in accordance with the constitutions $O{:}SNa\cdot O\cdot CH_2\cdot OH$ and $ONa\cdot S\cdot O\cdot CH_2\cdot OH$. Sodium hydrogen formaldehydesulphite has the formula $\mathrm{NaS}{<}^{\mathrm{O}}_{\mathrm{O\cdot CH_2\cdot OH}}$. Commercial sulphoxylate contains considerable quantities of sodium hydrogen sulphite, sodium sulphite, and also the substance $NaHSO_3\cdot CH_2O$. The compounds in which sulphur functions as a sexavalent element are more stable than those in which it is quadri- or bi-valent, consequently, where possible, there is always a tendency for the latter to pass into the former, thus:



$$OH\cdot\overset{O}{\overset{\|}{S}}\cdot ONa \longrightarrow Na\cdot\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\cdot ONa \quad\text{and}\quad ONa\cdot S\cdot OH \longrightarrow H\cdot\overset{O}{\overset{\|}{S}}\cdot ONa.$$

Z. K.

Production of a Sparingly Soluble [Basic] Zinc Formaldehydesulphoxylate. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 187494. Compare Abstr., 1906, i, 802).—One litre of 14% zinc hyposulphite solution at 70° is treated successively with 220 c.c. of 40% formaldehyde and 100 grams of zinc carbonate, the mixture being warmed and stirred until the reducing action of the solution has disappeared. The precipitated basic *zinc formaldehydesulphoxylate*, $OH\cdot Zn\cdot SO_2\cdot CH_2\cdot OH$, is then collected; it may be converted into the technically important sodium formaldehydesulphoxylate by treatment with sodium carbonate. The foregoing reaction takes the following course:

$$Zn(SO_2\cdot CH_2\cdot OH)_2 + Zn(OH)_2 = 2OH\cdot Zn\cdot SO_2\cdot CH_2\cdot OH,$$

and results in a separation of the sulphoxylate from soluble zinc formaldehydesulphite, which under these conditions remains unchanged. G. T. M.

Fission of Hydrogen Cyanide from Amides of α-Bromo-Fatty Acids Accompanied by the Formation of an Aldehyde or Ketone. Gustav Mossler (*Monatsh.*, 1908, **29**, 69—82).—The formation of aldehydes or ketones by the splitting off of formic acid from α-hydroxy-acids is a well-known reaction. In an analogous manner, as now found, the amides of α-bromo-acids when heated with aqueous or alcoholic sodium hydroxide lose hydrogen bromide and hydrogen cyanide, and form an aldehyde or ketone according to their configurations. The amides are best prepared by the action of ammonia on the α-bromo-acid bromide in benzene solution. In this manner have been prepared acetaldehyde, propaldehyde, *iso*butaldehyde, and benzaldehyde, acetone, and diethyl ketone; with 20% alcoholic potassium hydroxide, the yields obtained range from 40·4% to 97·4%, in the order in which the substances are named. G. Y.

Unimolecular Succindialdehyde. Carl D. Harries and Paul Hohenemser (*Ber.*, 1908, **41**, 255—260. Compare Abstr., 1901, i, 451; 1902, i, 345).—The glassy polymeric succindialdehyde does not yield the unimolecular variety on treatment with phosphoric oxide, but is completely destroyed (compare Abstr., 1907, i, 183). If, however, the polymerised form is distilled, the first fraction, below 169°, rejected as the dialdehyde in the distillate, contains water, and the fraction, b. p. 169—171°, then repeatedly distilled under reduced pressure, the unimolecular form of succindialdehyde is obtained as a mobile liquid, b. p. 56—57°/8—10 mm.; D^{21} 1·0642; mol. wt. in glacial acetic acid, 104—111, calc. 86; n_D^{19} 1·42717. The molecular refraction is therefore normal for a dialdehyde, but not for an enolic modification. The liquid, b. p. 65—66°/11 mm., earlier observed is always obtained when water is present (1901, *loc. cit.*).

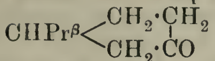
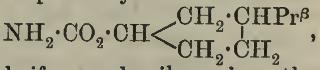
More careful determinations of the molecular refraction of the glassy and liquid forms at different temperatures show the conclusion previously drawn to be erroneous, that the transition temperature from M_5 to M_1 is 65° (1902, *loc. cit.*). Curves drawn connecting refractive index and temperature of both modifications intersect at 133°, and the dissociation temperature, although not determined, is therefore much higher than 65°.

The dielectric constant of the glassy form is 3·78, and that of the liquid form 28·5, temp. 20°, the aniline taken as the standard = 7·2.

In the preparation of succindialdehyde from the dialdoxime and nitrous fumes, it is important to use nitric acid of D 1·3; acid of D 1·4 leads to the formation almost exclusively of succinic acid. W. R.

A Synthesis of Certain Naturally-Occurring Aliphatic Ketones, and their Possible Mode of Formation in the Organism. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 4, 221—225).—An examination was made of certain ketones which are constituents of certain vegetable essential oils in order to see whether they can be prepared by oxidation of the corresponding saturated fatty acid in a manner analogous to the formation of acetone by the oxidation of butyric acid. The oxidation, as in previous work, was accomplished by means of hydrogen peroxide, and this type of β-oxidation occurs in the animal body. Experiment showed this could be done; thus lauric acid, after conversion into its ammonium salt and warming with hydrogen peroxide, readily yields methyl *n*-nonyl ketone, an unstable β-ketonic acid being its precursor. In a similar fashion, decoic acid yields methyl *n*-heptyl ketone, and octoic acid, methyl *n*-amyl ketone. These ketones probably arise in a corresponding way in the plant organism.

W. D. H.

New Derivatives of Camphenilone; its Constitution. LOUIS BOUVEAULT and GUSTAV BLANC (*Compt. rend.*, 1908, **146**, 233—235).—Dihydrocampholenamide (Semmler, Abstr., 1906, i, 681), obtained by the action of sodamide on camphenilone, yields on treatment with bromine and sodium methoxide (Jeffreys, Abstr., 1899, i, 730) the *urethane*, $C_8H_{15}\cdot NH\cdot CO_2Me$, b. p. 148°/17 mm., m. p. 26°. The *amine*, $C_8H_{15}\cdot NH_2$, obtained by heating the urethane at 120° with alcoholic potassium hydroxide, is a colourless liquid with a characteristic odour, b. p. 149°, and absorbs carbon dioxide from the air; when the hydrochloride is heated with potassium cyanate, it forms a crystalline *carbamide*, m. p. 163°, or when treated with sodium nitrite it is converted into the *alcohol*, $C_8H_{15}\cdot OH$, b. p. 81—82°/17 mm., and this on oxidation yields a *ketone*, b. p. 78—79°/17 mm, D_4^0 0·921, the *semicarbazone*, m. p. 198°, and *dibenzylidene* derivative, m. p. 143°, of which are identical with the corresponding derivatives of *iso*propyl*cyclo*pentane-3-one,  $CHPr^{\beta}<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CO\end{array}$ (Blanc, private communication). It follows, therefore, that the alcohol, amine, and amide described above are iso*propyl*cyclo*pentane-3-ol*, *3-amino*-1-iso*propyl*cyclo*pentane*, and iso*propyl*cyclo*pentane-3-carboxylamide* respectively. The formation of *iso*propyl*cyclo*pentane-3-carboxylamide,  $NH_2\cdot CO_2\cdot CH<\begin{array}{l}CH_2\cdot CHPr^{\beta}\\ CH_2\cdot CH_2\end{array}$, from camphenilone is readily explained if camphenilone has the constitution assigned to it by Wagner and Majewski (Abstr., 1900, i, 629). M. A. W.

Colorimetric Method of Determining the Molecular Size of Carbohydrates (Qualitative Demonstration of Aldehydes, Alcohols, and Carbohydrates). LEONHARD WACKER (*Ber.*, 1908, 41, 266—275).—The foundation of the method rests on the fact that phenylhydrazine-*p*-sulphonic acid in sodium hydroxide and in the presence of alcohols, acids, &c., develops a red colour in the air. It is found that (1) the intensity of the colour in equimolecular solutions is constant, and (2) that the velocity of the reaction is inversely proportional to the size of the molecule. The velocity is very different for differing classes of compounds; thus *N*/30,000 solution of formaldehyde or acetaldehyde develops the colour immediately, whilst *N*/2000 solutions of polyhydric alcohols and carbohydrates require fifteen minutes, primary alcohols require a strength of *N*/200, and concentrated solutions are required in the cases of acetone, lactic acid, citric acid, and proteins. The reaction in the cases of polyhydric alcohols and carbohydrates has been studied quantitatively, and from these determinations with compounds of known molecular weight it has been sought to determine the molecular weights of carbohydrates or pentosans. By comparing maltose with starch, amylodextrin, and erythrodextrin, it is, for instance, inferred that the molecular weights of starch and amylodextrin are identical ($?C_{36}H_{60}O_{30}$) and are three times that of maltose; that of erythrodextrin ($?C_{24}H_{40}O_{20}$) is twice that of maltose. Experiments carried out before and after inversion lead practically to the same conclusion. W. R.

Rate of Oxidation of Sugars in an Acid Medium. H. H. BUNZEL (*Amer. J. Physiol.*, 1908, 21, 23—36).—Sugars may be oxidised in an acid medium (*N*/2 acetic acid); the relative initial velocities of the oxidation are as follows for the sugars used: lactose (the slowest), 1·0; maltose, 1·15; dextrose, 5·71; galactose, 8·72; mannose, 8·72; lævulose, 55·13. These figures are believed to represent the relative amount of dissociation that occurs. Hydrogen ions retard the oxidation, because they decrease the total number of free oxygen ions in solution, and diminish the dissociation of the sugar molecule.

W. D. H.

C_5 Sugars from Meta- and Para-saccharin. HEINRICH KILIANI (*Ber.*, 1908, 41, 120—124. Compare Abstr., 1907, i, 1011).—The oximes of the C_5 sugars, obtained on reduction of meta- and parasaccharinic acid, were formerly shown to have identical properties. Crystallographic investigation proves them to be the same; a mixture of the two has m. p. 136°, and they both yield the same *tetrabenzoate*, m. p. 140°, crystallising in bunches of minute needles. The C_5 sugars from which the oximes were derived are also now shown to be the same; parasaccharopentose does not exist. They are crystallographically identical, whilst the difference in melting point formerly recorded is due to the deliquescence in moist air. The sugar from parasaccharinic acid is not a ketose, as, on oxidation with bromine, a butanetriolcarboxylic acid is formed, which yields the phenylhydrazide, m. p. 134°. It would appear that the β-ketose from parasaccharinic acid is extremely unstable, and is transformed into the aldose at the moment of its formation under the influence of the alkaline oxidising mixture.

E. F. A.

Transformation of *l*-Gulose and of *l*-Idose into *l*-Sorbose. WILLIAM ALBERDA VAN EKENSTEIN and JAN. J. BLANKSMA (*Rec. trav. chim.*, 1908, **27**, 1—4).—It has been shown that *d*-glucose and *d*-mannose are transformed by alkalis into lævulose (Lobry de Bruyn and Alberda van Ekenstein, Abstr., 1896, i, 116), that *d*-galactose and *d*-talose similarly are converted into *d*-tagatose (Abstr., 1898, i, 225), and that the latter sugar by migration of a hydroxyl group gives *l*-sorbose (Abstr., 1900, i, 332). Since *l*-sorbose is a ketose, yielding the same osazone as that obtained from *l*-gulose and *l*-idose, it is deduced theoretically that *l*-sorbose should be formed from *l*-gulose and *l*-idose by the action of alkali. The authors find this to be the case. According to Fischer's directions (Abstr., 1890, 1398), the mixture of *l*-gulonic and *l*-idonic acids is prepared from xylose, from this the former acid is separated as its lactone, and the latter by conversion into the dibenzylidene derivative. From the two acids, the corresponding sugars are obtained by reduction with sodium amalgam. When either of the sugar syrups so obtained is warmed with baryta, it is partly converted into *l*-sorbose, which can be isolated in a crystalline condition, having m. p. 165° and $a_D + 42·9°$ (in 1% aqueous solution). The authors find that *d*-sorbose, prepared from the juice of mountain ash berries by Freund's *Bacterium xylinum*, has m. p. 165° and $a_D - 42·9°$ (in 1% aqueous solution).

E. H.

The Phenomena of Fermentation from the Catalytic Point of View. H. SCHADE (*Biochem. Zeitsch.*, 1908, **7**, 299—326. Compare Abstr., 1906, i, 932).—Attention is drawn to the fact that many processes of fermentation, induced by enzymes, can be artificially accomplished by the aid of common hydrolysing materials. Examples mentioned are starch $\longrightarrow$ dextrose, sucrose $\longrightarrow$ dextrose and lævulose, lactose $\longrightarrow$ dextrose and galactose, glycogen $\longrightarrow$ dextrose, dextrose $\longrightarrow$ fatty acids, lævulose $\rightleftarrows$ dextrose, mannose $\rightleftarrows$ dextrose, and dextrose $\longrightarrow$ lactic acid. It is now shown that the conversion of lactic acid into alcohol and carbon dioxide can be accomplished by means of simple inorganic catalysts. Mineral acids convert lactic acid into a mixture of acetaldehyde and formic acid, and this mixture yields alcohol and carbon dioxide when passed over finely-divided rhodium (rhodium-black). Attention is drawn to the transformation of monoses under the influence of alkalis, and also to the probable formation of an intermediate product in the conversion of dextrose into lactic acid. The following scheme is given for the catalytic decomposition of monoses:

$$\begin{tikzcd}
\text{Dextrose} \arrow[r, shift left] & \text{lævulose} \arrow[l, shift left] \arrow[r, shift left] \arrow[d] & \text{mannose} \arrow[l, shift left] \\
 & \text{Intermediate product} \arrow[r] & \text{lactic acid} \\
 & & \text{Acetaldehyde and formic acid} \arrow[d] \\
 & & \text{Alcohol and carbon dioxide.}
\end{tikzcd}$$

It is suggested that whichever of the three monoses is used, it is the labile lævulose which undergoes decomposition.

The suggestion is also put forward that the various fermentations which sugar can undergo, for example, alcoholic, lactic, formic, &c., are essentially of the same type. The process in each case consists of several distinct reactions, and the function of any specific ferment is merely to accelerate one of these, so that the chief products obtained are the products formed by the accelerated reaction, whereas the products formed in the other reactions are obtained in small amounts only. J. J. S.

Some Mineral Salts which play the Part of Peroxydases.

Jules Wolff (*Compt. rend.*, 1908, **146**, 142—144).—Tincture of guaiacum which has become partially peroxidised with age, or the fresh tincture after treatment with a trace of hydrogen peroxide, but not before, gives a very intense blue coloration when added to a 0·01% ferrous sulphate solution. The reaction is observed with a solution containing only one part of ferrous sulphate per million, a quantity which cannot be detected by potassium ferricyanide. The dilute ferrous sulphate solution loses its activity when boiled with a trace of hydrogen peroxide, being oxidised to ferric sulphate, which does not act on guaiacum after boiling. The reaction is very similar to those produced by different vegetable extracts, such as those of malt, barley, and wheat, containing a peroxydase, and, like them, is inhibited by very small quantities of mineral acids.

Small quantities of ferrous, ferric, and cupric sulphates in the presence of traces of hydrogen peroxide are capable of oxidising certain colouring matters and of liquefying starch. Thus dilute solutions of methyl-orange, methylene-blue, and magenta are decolorised by ferrous sulphate at the ordinary temperature, of ferric sulphate at 50°, and of cupric sulphate on boiling, in solutions containing 0·1—0·2 gram of anhydrous salt per litre and small quantities of hydrogen peroxide, whilst 50 c.c. of a 5% solution of starch are liquefied in 25 minutes at 70° by addition of 0·002 gram of ferrous sulphate and a quantity of hydrogen peroxide containing 0·0028 gram of active oxygen. In the latter reaction, cupric sulphate is twice as active as the ferrous salt.

These phenomena, which occur without the evolution of oxygen, cannot be of a catalytic nature, since hydrogen peroxide has not the same power of decolorising dyes and liquefying starch when in conjunction with platinum-black.

As in the saccharification by amylase (Fernbach) and the diastatic liquefaction of starch, the solutions of iron salts have the highest liquefying power when their reaction is approximately neutral to methyl-orange. E. H.

Colloidal Properties of Starch and the Existence of a Perfect Solution of this Substance. EUGÈNE FOUARD (*Compt. rend.* 1908, **146**, 285—287. Compare Abstr., 1907, i, 391, 677).—A 5% pseudo-solution of demineralised and partially hydrated starch, prepared at 80°, is filtered through a collodion membrane. The filtrate contains 2·74% of starch, and from its properties seems to be a true solution as distinguished from the colloidal solutions of the so-called "soluble starch." Thus the solution does not polarise light, is not acted on by an electric current, and has a viscosity only slightly greater than an equivalent solution of sucrose (an ordinary starch "solution" has a viscosity ten times as great). When treated with iodine, the solution gives an intense blue coloration, but no precipitate. The extreme dissemination of the starch molecules in this "true solution" is shown by its complete hydrolysis in five minutes when heated with 10% of hydrogen chloride on a boiling water-bath, an ordinary starch "solution" of the same strength being incompletely saccharified by six hours' similar treatment.

When kept, the "true solution" becomes very slightly opalescent, and this opalescence settles slowly, forming a slight pulverulent deposit consisting of very refringent spherical or ovoid granules, 2—3μ in diameter, similar to the natural starch grains. The same granular transformation can be effected either by freezing or by evaporation in a vacuum.

The opalescence disappears on boiling. If a new "true solution" of starch containing 2·346% and having $[\alpha]_D$ 186°6′ is treated with one-quarter of its volume of water and boiled for fifteen minutes at a constant volume, it remains equally limpid, undergoes no saccharification, but $[\alpha]_D$ increases to 193°36′.

The conclusion is drawn that dissolved starch molecules occur in the ordinary colloidal solution, accompanied by starch in all degrees of molecular condensation. E. H.

The Chemistry of the Bleaching of Sulphite-Cellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1908, **21**, 302—303).—In order to test Cross and Bevan's theory (*J. Soc. Chem. Ind.*, 1890, 450) that during the process of bleaching some cellulose is chlorinated, the author has made a number of chlorine determinations both in the bleaching agents and in the fibre, and finds that practically no chlorination takes place. P. H.

Action of *n*-Propyl Chloride on Ethylamine. EZIO COMANDUCCI and M. ARENA (*Chem. Zentr.*, 1907, ii, 1396; from *Giorn. Farm. Chim.*, 1907, **56**, 385—388).—The product obtained by the action of *n*-propyl chloride on ethylamine in molecular proportions in aqueous solution in a sealed tube at 125—140° contains three parts of ethyl-*n*-propylamine and one part of ethyldi-*n*-propylamine.

Ethyl-n-*propylamine*, NHEtPr, is a colourless, refracting liquid, b. p. 79·8°/747 mm., D^{24} 0·773; the *hydrochloride*, m. p. 217—218°; the *aurichloride*, m. p. 86—87°; the *platinichloride*, orange-yellow needles, m. p. 198—199°. The *nitroso*-derivative is obtained as a greenish-yellow oil, b. p. 195°.

Ethyldi-n-*propylamine*, $NEtPr_2$, is a colourless liquid, b. p. 137·2°/749·9 mm., D^{24} 0·807; the *hydrochloride*, m. p. 113—115°; the *aurichloride*, m. p. 93—94°; the yellow, crystalline *platinichloride*, m. p. 175°. G. Y.

White Precipitate. ERNST SCHMIDT [with L. KRAUSS] (*Chem. Zentr.*, 1907, ii, 1593; from *Zeitsch. Öesterr. Apoth.-Ver.*, 1907, **45**, 541—543).—The constitution of fusible and infusible white precipitates, the composition of which appears to vary within certain limits with the method of preparation, has been the object of numerous investigations. A résumé of the views of various authors and an account of a study of the action of methyl iodide are given.

When heated with methyl iodide, with or without addition of methyl alcohol, in a sealed tube at 100°, infusible white precipitate forms tetramethylammonium mercuric iodide, NMe_4I,HgI_2 (Risse, *Annalen*, 1858, **107**, 223), which, after precipitation of the mercury by means of hydrogen sulphide, yields the *aurichloride*, NMe_4AuCl_4, crystallising in long, yellow needles. At the ordinary temperature, the action of methyl iodide on infusible white precipitate leads to the formation of the iodide, $2NMe_4I,3HgI_2$ (Risse, *loc. cit.*), m. p. 187°, which is formed also by heating the preceding iodide with mercuric iodide. A third, yellow, crystalline *iodide*, m. p. 110°, obtained from the mother liquors, gives a red coloration with lime, becoming yellow on exposure to air, and yields mercuric iodide when treated with water.

Under the same conditions, fusible white precipitate yields tetramethylammonium mercuric iodide, NMe_4I,HgI_2, only. G. Y.

The Order of the Addition of Ammonia to Organic *as-a*-**Oxides.** K. KRASSUSKY (*Compt. rend.*, 1908, **146**, 236—239. Compare Wurtz, *Ann. Chim. Phys.*, 1857, [iii], **49**, 381; Knorr, Abstr., 1897, i, 313; 1899, i, 461).—β-Methyl-Δ^{β}-butylene oxide does not combine with anhydrous ammonia, but when heated in sealed tubes at 100° with a 33% solution of ammonia it yields *dimethyl a-aminoethylcarbinol*, $NH_2\cdot CHMe\cdot CMe_2\cdot OH$, b. p. 157—158°/743 mm., m. p. 26°, D^{15} 0·9291 or D^{20} 0·9251, which forms hygroscopic, crystalline salts, and a *platinichloride* in large, orange-red prisms. The constitution of this amino-alcohol has been determined by its synthesis from the ethyl ester of alanine and magnesium methyl iodide,

$$NH_2\cdot CHMe\cdot CO_2Et \longrightarrow NH_2\cdot CHMe\cdot CMe_2\cdot OH,$$

and the same compound is also obtained by the action of ammonia on β-methyl-Δ^{β}-butylene chlorohydrin, but in this reaction β-methyl-Δ^{β}-butylene oxide is formed as an intermediate compound.

*iso*Butylene oxide combines with aqueous ammonia to form *aminotrimethylcarbinol*, $NH_2\cdot CH_2\cdot CMe_2\cdot OH$, b. p. 150·5—151·5°/762 mm.,

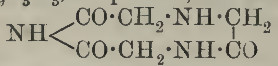
D^0 0·9500 or D^{14} 0·9389; the *platinichloride* forms red, prismatic needles; this alcohol is identical with the synthetic compound obtained by the action of magnesium methyl iodide on the ethyl ester of glycine. It follows, therefore, that *as*-α-oxides combine with ammonia to form amino-alcohols in which the hydroxyl is attached to the carbon atom, which in the original compound was associated with the least number of hydrogen atoms.

In addition to the amino-alcohols just described, β-methyl-Δ^β-butylene and *iso*butylene oxides yield with ammonia the secondary hydroxyamines, $(C_5H_{11}O)_2NH$ and $(C_4H_9O)_2NH$, respectively.

M. A. W.

New Compounds of Amino-acids and Ammonia. II.

PETER BERGELL and JOHANNES FEIGL (*Zeitsch. physiol. Chem.*, 1908, **54**, 258—287).—Diglycinimide (Abstr., 1907, i, 394) has been further investigated; it is extremely stable towards mineral acids even at 120°, but is decomposed very readily by cold alkalis, although definite products could not be isolated. It has been found possible to obtain acyl derivatives of the imide by the reaction of certain acyl chlorides in the presence of magnesium oxide or sodium hydrogen carbonate, and the products of hydrolysis of these acyl derivatives confirm the constitution of the imide arrived at previously, for example, benzoyldiglycinimide yields hippuric acid, glycine, and ammonia.

Chloroacetyldiglycinimide reacts with ammonia, yielding a *compound*, $C_6H_9O_3N_3$, m. p. 228°, which in all probability has the cyclic constitution  $NH<\begin{array}{l}CO\cdot CH_2\cdot NH\cdot CH_2\\ \qquad\qquad\qquad\quad |\\ CO\cdot CH_2\cdot NH\cdot CO\end{array}$ (compare Zelinsky, Abstr., 1907, i, 780).

Homologues of diglycinimide have been prepared, for example, alaninglycinimide, by the action of ammonia on the product obtained by the condensation of chloroacetic acid and α-chloropropionitrile.

Diglycinimide platinichloride, $(C_4H_9O_2N_3)_2PtCl_6$, crystallises from water in well-developed, prismatic plates. Double salts with cadmium chloride and mercuric chloride have been obtained, and also a crystalline phosphomolybdate and an amorphous phosphotungstate. The *picrate*, $C_4H_9O_2N_3,C_6H_4O_7N_3$, crystallises from dilute alcohol in long, plastic needles, m. p. 231°. The *picrolonate*, $C_4H_9O_2N_3,C_{10}H_8O_5N_4$, crystallises in pointed plates, which decompose at 212°. *Benzoyldiglycinimide*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot COPh$, crystallises from alcohol in microcrystalline aggregates, m. p. 231°, and is not basic in nature.

Carbethoxydiglycinimide, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot CO_2Et$, obtained by the action of ethyl chlorocarbonate on diglycinimide hydrochloride in the presence of sodium hydrogen carbonate, crystallises from alcohol in colourless plates, m. p. 172°, and is decomposed when boiled with water. *Chloroacetyldiglycinimide*,

$$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl,$$

crystallises from alcohol in colourless prisms, m. p. 174°.

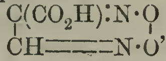
Full details for the preparation of chloropropionitrile by the action of phosphorus pentachloride on lactonitrile are given. The nitrile condenses with dry chloroacetic acid at 103° in a shaking-oven, yielding *methyldichlorodiacetimide*, $CH_2Cl·CO·NH·CO·CHMeCl$, which crystallises from a mixture of benzene and light petroleum in felted needles, m. p. 108°. The chloro-derivative reacts with ammonia at low temperatures, yielding *alaninglycinimide*,

$$NH_2·CH_2·CO·NH·CO·CHMe·NH_2.$$

The *hydrochloride* is precipitated by the addition of alcohol to its aqueous solution in the form of slender needles, m. p. 236°.

J. J. S.

Ethyl Dioximinosuccinate. Action of Nitric Acid on Ethyl Dioximinosuccinate. André Wahl (*Bull. Soc. chim.*, 1908, [iv], 3, 22—27, 27—31).—Most of the facts recorded in these two papers have been published already (Abstr., 1906, i, 624; 1907, i, 493). Ethyl dioxysuccinate, b. p. 120—125°/13 mm., in contact with water forms a *hydrate*, m. p. 133°, which separates from ether in small prisms. In preparing ethyl dioximinosuccinate from ethyl dioxysuccinate there is formed, in addition to the by-products already recorded, some ethyl tartronate.

Ethyl glyoxime-peroxide-dicarboxylate, $C_8H_{10}N_2O_6$, produced by the action of nitric acid on ethyl dioximinosuccinate (Beckh, Abstr., 1897, i, 213) on treatment with ammonia, yields an amide, m. p. 250°, concerning the properties of which many discrepant statements have been made (Pröpper, Abstr., 1883, 573; Cramer, Abstr., 1892, i, 699; Beckh, *ibid.*, 1897, i, 213; Bouveault and Bongert, *Bull. Soc. chim.*, 1902, 27, 1170; Ulpiani and Bernardini, Abstr., 1904, i, 971; 1905, i, 750; Wieland, *ibid.*, 1907, i, 527). Determination of its molecular weight by ebullioscopic methods indicates that it has the empirical formula $(CONH)_3$, and may, therefore, be the amide of the acid, , described by Jovitschitsch (Abstr., 1906, i, 733).

T. A. H.

Platinum-Blue. Karl A. Hofmann and Günther Bugge (*Ber.*, 1908, 41, 312—314. Compare Abstr., 1907, i, 489).—The blue solution obtained by the action of silver nitrate on platinous chloride bisacetonitrile contains *platinous acetamide*, and the crystalline compound, $Pt(NHAc)_2,H_2O$, may be isolated by shaking a mixture of equal weights of silver sulphate and platinous chloride bisacetonitrile with five times its weight of water, adding methyl alcohol, filtering, and precipitating the filtrate with ether. The same compound can be prepared directly from acetamide and potassium platinochloride by the addition of silver nitrate. Other salts which yield acids in the presence of platinous chloride can be used in place of silver nitrate, and it is not necessary actually to isolate the acetonitrile platinochloride. The compound can be prepared from a mixture of the nitrile and potassium platinochloride by the action of a solution of sodium acetate.

J. J. S.

Dimethylol Compounds of Carbamide. Alfred Einhorn and Alexander Hamburger (*Ber.*, 1908, 41, 24—28).—The fact that the *N*-methylol compounds, prepared by Einhorn (Abstr., 1906, i, 245) from acid amides, are all extremely well-characterised, crystalline substances, suggested that Goldschmidt's dimethylolcarbamide (Abstr., 1898, i, 178) required re-investigation. Repetition of his work has shown that the white, amorphous precipitate, obtained by the action of carbamide on formaldehyde in the presence of potassium hydroxide, and assumed to be dimethylolcarbamide, varies in composition with the concentration of the alkali. *Dimethylolcarbamide*, $CO(NH\cdot CH_2\cdot OH)_2$, can, however, be obtained if barium hydroxide is employed, and the reaction stopped when Tollens' silver solution is no longer instantly reduced by saturating the solution with carbon dioxide. It crystallises in small, well-defined prisms, sinters at 121°, m. p. 126°, becomes solid again at 137—138°, and then decomp. at 260°. When heated, it evolves formaldehyde, and forms basic decomposition products; it gradually reduces Tollens' silver solution. Amorphous condensation products of varying composition are formed when a solution in water is treated with 1% potassium carbonate, but one of the constituents may result from the removal of the elements of water from two molecules of dimethylolcarbamide.

Monomethylolcarbamide, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot OH$, prepared when only half the quantity of formaldehyde is employed, has not yet been obtained quite pure, and crystallises in rosettes of prisms, m. p. 116°. Dilute mineral acids instantly, and alkalis slowly, cause separation of amorphous precipitates of variable composition. W. R.

Constitution of Thioamides. EINAR BIILMANN (*Chem. Zentr.*, 1907, ii, 1778—1780; from *Oversigt Danske Videns. Selskabs Forhandl.*, 1907, 83—104. Compare Abstr., 1905, i, 625).—Tautomerism has been ascribed to the thioamides chiefly because of the formation of iminothiol ethers, $\cdot C(SR){:}NH$, and thiolurethanes, $NH_2\cdot CO\cdot SR$, by the action of alkyl iodides on thioamides, $\cdot CS\cdot NH_2$, and thionurethanes, $NH_2\cdot CS\cdot OR'$, which are considered to react in the tautomeric forms, $\cdot C(SH){:}NH$ and $NH{:}C(SH)\cdot OR'$, respectively. This explanation, however, assumes the direct interaction of the free thiol group, SH, and the alkyl iodide, whereas no case is known of the direct alkylation of an undoubted thiol group. On the other hand, it is now shown that alkylation of a thiocarbonyl group may take place in the absence of a mobile hydrogen atom. Xanthylacetic acid and bromoacetic acid interact at 120°, yielding ethyl bromide and dithiolcarbonateacetic acid. This reaction must take place in the two stages: $OEt\cdot CS\cdot S\cdot CH_2\cdot CO_2H + CH_2Br\cdot CO_2H =$

$$OEt\cdot CBr(S\cdot CH_2\cdot CO_2H)_2 = CO(S\cdot CH_2\cdot CO_2H)_2 + EtBr.$$

In the same manner, β-xanthylpropionic acid and β-iodopropionic acid form β-dithiolcarbonatepropionic acid, $CO(S\cdot CH_2\cdot CH_2\cdot CO_2H)_2$, and ethyl iodide. The yields are not quantitative, partly, at least, because the ethyl haloid, formed during the reaction, reacts with the xanthate; thus the action of ethyl iodide on xanthylacetic acid leads to the formation of ethyldithiolcarbonateacetic acid, $SEt\cdot CO\cdot S\cdot CH_2\cdot CO_2H$. Similar reactions take place with xanthylacetic acid and diphenylmethyl bromide, forming diphenylmethyldithiolcarbonateacetic acid, and with diphenylmethyl bromide and potassium xanthate, forming ethyl diphenylmethylxanthate and, by action of a further mol. of the bromide, diphenylmethyl dithiolcarbonate.

It is argued that, in analogy with these reactions, the action of alkyl haloids on thioamides and thionurethanes must take place in two stages, the first being an addition of the alkyl haloid to the thiocarbonyl group (compare Wheeler and Barnes, Abstr., 1900, i, 564).

Dithiolcarbonateacetic acid, $C_5H_6O_5S_2$, forms white crystals, m. p. 156·6° (corr.); the *ethyl* ester, $C_9H_{14}O_5S_2$, white needles, m. p. 49·2°. *β-Dithiolcarbonatepropionic acid*, $C_7H_{10}O_5S_2$, white needles, m. p. 115—116°, when heated with alcoholic sodium hydroxide, yields thiohydracrylic acid and sodium carbonate.

Diphenylmethyl dithiolcarbonateacetic acid, $CHPh_2·S·CO·S·CH_2·CO_2H$, forms crystals, m. p. 130·6°, and on treatment with alcoholic sodium hydroxide, yields thiobenzhydrol, sodium thioglycollate, and sodium carbonate.

Diphenylmethyl dithiolcarbonate, $CO(S·CHPh_2)_2$, crystallises in white needles, m. p. 135·8°, forms an intensely blue *substance* (*thiobenzophenone*?) when heated, and yields thiobenzhydrol and sodium carbonate on treatment with alcoholic sodium hydroxide. Oxidation of the alkaline solution with iodine leads to the formation of *diphenylmethyl disulphide*, $S_2(CHPh_2)_2$, m. p. 152°. G. Y.

Influence of Addition of Chloride on the Reaction between Barium Carbonate, Carbon, and Nitrogen. OTTO KÜHLING and O. BERKHOLD (*Ber.*, 1908, 41, 28—32. Compare Abstr., 1907, ii, 166).—Pure barium carbonate (1 mol.) and sugar charcoal were well mixed with 2, 5, 10, 15, 20, and 30% of barium chloride and placed in unglazed porcelain boats heated in porcelain tubes in an electric furnace at 920—1180°. Nitrogen, free from carbon dioxide, moisture, and oxygen, was passed over the heated mixture for one hour, and the product analysed. As a result, it was ascertained that (1) more than 2% barium chloride lowers the temperature at which the nitrogen begins to be absorbed; (2) there is no quantitative relationship between temperature of combination and quantity of chloride; (3) the yield of cyanide falls as the barium chloride is increased, with small quantities the yield is either the same or very little smaller, and (4) the yield of cyanamide is, however, smaller throughout. W. R.

Action of Sulphuric Acid on Calcium Cyanamide. TEMISTOCLE JONA (*Gazzetta*, 1907, 37, ii, 558—562).—The action of sulphuric acid on calcium cyanamide (compare E. Pollacci and G. Pollacci, *Staz. sper. agrar. ital.*, 1907, 40, 580—592) yields calcium and ammonium sulphates and dicyanodiamidine,

$$NH_2·C(NH)·NH·CO·NH_2.$$

T. H. P.

Reactivity of Mercuric Cyanide. KARL A. HOFMANN and H. WAGNER (*Ber.*, 1908, 41, 317—321).—Although an aqueous solution of mercuric cyanide is practically a non-electrolyte, it reacts with aqueous solutions of silver acetate or nitrite, yielding precipitates of silver cyanide. The precipitation is not complete, as the reaction is reversible, and the amount precipitated depends largely on the concentration of the solutions. Silver nitrate does not yield a precipitate in dilute solutions, and with concentrated solutions the sparingly soluble compound, $HgC_2N_2,AgNO_3,2H_2O$, is deposited. Silver sulphate produces a precipitate, but not to the same extent as the nitrite and acetate.

The double cyanide-acetate, $HgC_2N_2,Hg(OAc)_2$, may be prepared from the two components; it crystallises in long, pointed, doubly-refracting prisms, and its clear aqueous solution gives a cloudiness with a large excess of silver acetate.

Mercuric cyanide is much more soluble in potassium hydroxide solution than in water, and the solution obtained reacts as an oxidising agent towards alcohol, glycerol, dextrose, quinol, and gallic acid. It reacts with benzaldehyde and benzoin, yielding precipitates of mercury, and with picric acid yields potassium *iso*purpurate. Crystals having the composition HgC_2N_2,KOH,H_2O have been isolated from the solution. They dissolve readily in water, yielding a strongly alkaline solution, and the addition of silver nitrate produces a precipitate of silver cyanide.

A compound, HgC_2N_2,KOH, has also been isolated; it crystallises in colourless, rhombic plates. Finely-divided mercuric cyanide reacts with a saturated solution of potassium hydroxide, yielding yellow mercuric oxide, but, when diluted with water, a clear solution is obtained. J. J. S.

Action of Hydrazine on Diazoacetamide and on Ethyl Diazoacetate. Theodor Curtius, August Darapsky, and August Bockmühl (*Ber.*, 1908, 41, 344—356).—Diazoacetamide reacts readily with hydrazine hydrate, yielding ammonia and *azoimideacetylhydrazide*, $N_3{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, which may be isolated in the form of its *benzylidene* derivative, $N_3{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh$. The same compound can be obtained by the action of excess of free hydrazine on ethyl diazoacetate, and its constitution follows from its synthetical formation from ethyl azoimideacetate, which can be prepared from silver azoimide and ethyl iodoacetate. When warmed with moderately concentrated sulphuric acid, the condensation product yields nitrogen and hydrazine sulphate. The reaction between ethyl diazoacetate and hydrazine is represented by the following equations: $NH_2{\cdot}NH_2 + N_2{:}CH{\cdot}CO_2Et \longrightarrow NH_2{\cdot}NH{\cdot}N{:}N{\cdot}CH_2{\cdot}CO_2Et \longrightarrow NH_3 + N_3{\cdot}CH_2{\cdot}CO_2Et$ and $N_3{\cdot}CH_2{\cdot}CO_2Et + NH_2{\cdot}NH_2 \longrightarrow$

$$N_3{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2 + EtOH.$$

Diazoacetamide (27% yield) (Abstr., 1884, 988) is obtained by shaking methyl diazoacetate with 10% ammonium hydroxide until a clear solution is obtained, and keeping this at the ordinary temperature for three months.

Benzylideneazoimideacetylhydrazide crystallises from alcohol in long, felted needles, m. p. 149° (decomp.). In the preparation of this compound, a small amount of benzaldazine is obtained, but may be removed by washing the benzylidene derivative with ether.

Ethyl azoimideacetate is most readily freed from excess of ethyl iodoacetate by means of diethylamine; it is a colourless oil, b. p. 75°/21 mm.

Azoimideacetylhydrazide hydrochloride may be obtained by hydrolysing the benzylidene compound with cold concentrated hydrochloric acid, and forms an extremely deliquescent, crystalline mass. *Azoimideacetylazoimide*, $N_3{\cdot}CH_2{\cdot}CO{\cdot}N_3$, is a colourless oil with a penetrating odour, is insoluble in water, and is hydrolysed by potassium hydroxide solution to potassium azoimideacetate and potassium azoimide.

The *sodium*, *barium*, and *silver* salts of azoimideacetic acid have been prepared. The free acid forms a colourless oil with a penetrating odour, and dissolves in water, yielding a strongly acidic solution.

Sulphuric acid hydrolyses ethyl azoimideacetate, forming nitrogen, ammonia, and formaldehyde; potassium hydroxide yields nitrogen, ammonia, and oxalic acid. J. J. S.

Methyl Ester and Hydrazide of Nitrosoiminoacetic Acid. Theodor Curtius, August Darapsky, and Ernst Müller (*Ber.*, 1908, **41**, 356—358).—Commercial glycine methyl ester contains *methyl iminoacetate*, $NH(CH_2{\cdot}CO_2Me)_2$, and this with nitrous acid yields the *nitroso*-derivative, $NO{\cdot}N(CH_2{\cdot}CO_2Me_2)_2$, which is therefore contained in commercial ethyl diazoacetate prepared from glycine methyl ester. The nitroso-derivative is a thick, yellow oil, b. p. 162°/17 mm., and reacts with hydrazine hydrate, yielding the corresponding *hydrazide*, $NO{\cdot}N(CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2)_2$, which crystallises from warm water in large, glistening plates, m. p. 175° (decomp.). It gives Liebermann's reaction, and, when boiled with dilute sulphuric acids, yields azoimide. The *dibenzylidene* derivative of the hydrazide,

$$NO{\cdot}N(CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh)_2,$$

has m. p. 215° (decomp.), and is practically insoluble in the ordinary solvents. The *azoimide*, $NO{\cdot}N(CH_2{\cdot}CO{\cdot}N_3)_2$, is a yellow oil with a penetrating odour. J. J. S.

Action of Alkaline Mercuric Cyanide on Halogen Derivatives of Ethylene and Acetylene. Karl A. Hofmann and H. Kirmreuther (*Ber.*, 1908, **41**, 314—317).—Mercury acetylide is formed when pure acetylene is passed into an aqueous solution of mercuric cyanide to which a small amount of potassium hydroxide has been added. In the absence of the alkali, a precipitate is not formed. A solution of 50 grams of the cyanide and 23 grams of potassium hydroxide in 200 grams of water is an energetic reagent for the removal of hydrogen halides, and in certain cases for replacing hydrogen by mercury.

Mercuric tribromoethylene, $Hg(CBr{:}CBr_2)_2$, is obtained when acetylene tetrabromide is shaken with the above solution for some ten hours. Crystals of HgC_2N_2,KBr,H_2O are deposited, and a certain amount of dibromoacetylidene is also formed. The tribromo-derivative crystallises from ether in colourless, doubly-refractive prisms, m. p. 141°. When shaken with yellow ammonium sulphide, it yields tribromoethylene, but is not decomposed when boiled with water or 10% hydrochloric acid.

Mercuric trichloroethylene, $Hg(CCl{:}CCl_2)_2$, is most readily obtained by shaking trichloroethylene with the cyanide solution, and has m. p. 83°.

Mercuric chloroacetylene, $Hg(C{:}CCl)_2$, is formed when the gas obtained by heating trichloroethylene with alcoholic potassium hydroxide is washed with water and concentrated sulphuric acid, and then led into the cyanide solution. It is deposited as a white precipitate, and crystallises from ether in glistening plates, m. p. 185°. It decomposes at 195°, but is not attacked by concentrated hydrochloric acid. J. J. S.

Influences Governing Orientation in the Benzene Nucleus. Julius Obermiller (*J. pr. Chem.*, 1908, [ii], 77, 65—84. Compare Abstr., 1907, i, 200).—A reply to the criticisms of Flürscheim (Abstr., 1907, i, 834). G. Y.

Chemical Dynamics of the Bromination of Toluene. Ludwik Bruner and Mlle. J. Dluska (*Bull. Acad. Sci. Cracow*, 1907, 691—730. Compare Bruner, 1902, ii, 447).—A study of the action of small amounts of bromine on toluene alone and in presence of a solvent.

It is found that in absence of a solvent and with the concentration of the bromine not greater than 1 mol. per 30 mols. of toluene, the bromination of toluene is a unimolecular reaction, the substitution in the nucleus and that in the side-chain being independent reactions. At temperatures between 0° and 74°, the distribution of the bromine between the two side reactions does not vary with the concentration. For the temperature interval, 25—35°, the nucleus substitution has a temperature-coefficient, 1·3—1·5; the side-chain substitution, a coefficient usually greater than 4·0. The nucleus substitution is accelerated by iodine bromide in proportion to the square of the concentration of this halogen carrier; the lower the temperature at which the bromination takes place, the wider the concentration limits within which this rule holds good, whilst it ceases to apply to reactions above about 35°. The temperature-coefficient, 1·0—1·2, of the catalysis is notably small.

The distribution of the bromine between the nucleus and the side-chain and the unimolecular nature of the reaction are maintained in carbon tetrachloride solution, but the velocity of the reaction is diminished very nearly in proportion to the diminution of the toluene concentration. In nitrobenzene solution, on the other hand, the reaction is hindered probably by the hydrogen bromide formed, and the yield of benzyl bromide is markedly diminished; hence the nitrobenzene favours the nucleus substitution as does the halogen carrier. The velocity of the bromination of the side-chain under the influence of light also varies with the solvent, being accelerated by associating mediums, but diminished by solvents, such as nitrobenzene, amyl acetate, and acetic acid, which favour dissociation of the halogen. The retardation of the reaction in nitrobenzene cannot be caused by protection of the reacting substances from the light by the solvent, since toluene decolorises bromine instantaneously on exposure to sunlight even when the reaction mixture is jacketed with nitrobenzene.

It is argued that the course of the bromination depends on the extent to which the bromine is electrolytically dissociated, the side-chain substitution being a reaction of bromine molecules, and the nucleus substitution one of bromine or iodine bromide ions. G. Y.

Nitration of *s-m*-Dichloro- and *s-m*-Dibromo-nitrobenzene. JAN J. BLANKSMA (*Rec. trav. chim.*, 1908, **27**, 42—48. Compare Abstr., 1906, i, 11).—Unlike *s*-nitro-*m*-xylene, *s*-dibromonitrobenzene is only slowly nitrated by nitric acid, D 1·52, but, when heated on a water-bath with a mixture of the latter and sulphuric acid, it forms 1 : 3-*dibromo*-4 : 5-*dinitrobenzene*, $C_6H_2Br_2(NO_2)_2$, as colourless crystals, m. p. 86°, of which the constitution is fixed by the formation of 4 : 6-dibromo-2-nitroaniline when heated with alcoholic ammonia in a sealed tube. 1 : 3-Dibromo-4 : 5-dinitrobenzene gives 4 : 6-dibromo-2-nitrophenol when heated with alkali hydroxide solution, 4 : 6-dibromo-2-nitrophenyl methyl ether (Körner, Abstr., 1876, 204) by the action of sodium methoxide, 4 : 6-dibromo-2-nitromethylaniline (Blanksma, Abstr., 1902, i, 600) when heated with alcoholic methylamine, 4 : 6-*dibromo-2-nitrodiphenylamine*,

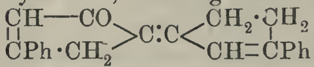
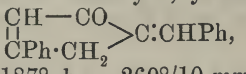
$$NHPh\cdot C_6H_2Br_2\cdot NO_2,$$

orange-red crystals, m. p. 80°, by heating with aniline, 4 : 6 : 4′ : 6′-*tetrabromo*-2 : 2′-*dinitrodiphenyl sulphide*, $S(C_6H_2Br_2\cdot NO_2)_2$, a yellow powder, m. p. 90° (approx.), by the action of sodium sulphide, and 4 : 6 : 4′ : 6′-*tetrabromo*-2 : 2′-*dinitrodiphenyl disulphide*, $S_2(C_6H_2Br_2\cdot NO_2)_2$, brilliant yellow crystals, m. p. 207°, with sodium disulphide. By oxidation with nitric acid, the latter derivative gives 4 : 6-dibromo-2-nitrobenzenesulphonic acid.

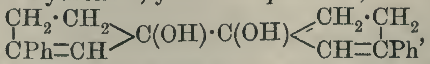
Similarly, *s*-dichloronitrobenzene gives 1 : 3-*dichloro*-4 : 5-*dinitrobenzene*, which forms crystals, m. p. 98°. The constitution of this chloro-derivative is also determined by the production of 4 : 6-dichloro-2-nitroaniline. By treatment with the reagents mentioned above, 1 : 3-dichloro-4 : 5-dinitrobenzene gives 4 : 6-dichloro-2-nitrophenol, 4 : 6-dichloro-2-nitrophenyl methyl ether, 4 : 6-*dichloro-2-nitromethylaniline*, $NHMe\cdot C_6H_2Cl_2\cdot NO_2$, orange-red crystals, m. p. 80°, 4 : 6-*dichloro-2-nitrodiphenylamine*, $NHPh\cdot C_6H_2Cl_2\cdot NO_2$, yellow crystals, m. p. 72°, 4 : 6 : 4′ : 6′-*tetrachloro*-2 : 2′-*dinitrodiphenyl sulphide*, m. p. 70—80°, and 4 : 6 : 4′ : 6′-*tetrachloro*-2 : 2′-*dinitrodiphenyl disulphide*, $S_2(C_6H_2Cl_2\cdot NO_2)_2$, yellow crystals, m. p. 190°. The latter compound is oxidised by nitric acid to 4 : 6-dichloro-2-nitrobenzenesulphonic acid. E. H.

The Question of the Miscibility and Form-Analogy in Aromatic Nitro- and Nitroso-compounds. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1907 (1908), **10**, 436—440).—Crystallographic determinations are given of *o*-nitroacetanilide and of *o*-nitrosoacetanilide; both are monoclinic, with $a:b:c = 0·8935:1:1·9198$ and $a:b:c = 0·8940:1:0·7295$ repectively. There is thus a similarity in the ratio of $a:b$. The two substances appear to be capable of mixing in solid solution to only a limited extent. L. J. S.

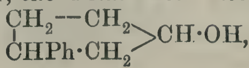
The Phenyl*cyclo*pentane Group. WALTHER BORSCHE and W. MENZ [in part, ALBERT FELS] (*Ber.*, 1908, **41**, 190—210).—Members of the phenyl*cyclo*pentane group have not hitherto been subjected to a thorough investigation. The hydrocarbon itself is obtained from 1-phenyl-Δ^1-*cyclo*pentene-3-one by way of 1-phenyl*cyclo*pentane-3-ol, 1-phenyl-3-bromo*cyclo*pentane, and 1-phenyl*cyclo*pentane-3-carboxylic acid. The compound described by Paal (Abstr., 1884, 1177) as dehydrophenacylacetone is undoubtedly 1-phenyl-Δ^1-*cyclo*pentene-3-one as stated by Borsche and Fels (Abstr., 1906, i, 509), for on reduction it is converted into a saturated alcohol, which yields on oxidation a ketone containing the group $-CH_2\cdot CO\cdot CH_2-$, since it condenses with benzaldehyde yielding a dibenzylidene derivative.

1-Phenyl-Δ^1-*cyclo*pentene-3-one is formed together with β-benzoylpropionic acid on warming ethyl phenacylacetoacetate with 2% aqueous sodium hydroxide solution; it may also be prepared by treating phenacylacetone with 2% aqueous sodium hydroxide or by boiling phenuvic acid with strong hydrochloric acid. The *hydrochloride*, $C_{11}H_{10}O,HCl$, forms bright red crystals, sinters at 62°, m. p. 68—69°; the *platinichloride*, $(C_{11}H_{10}O)_2,H_2PtCl_6,2H_2O$, forms slender, orange-yellow needles, decomposing above 145°; the *aurichloride*, $C_{22}H_{20}O_2,HAuCl_4$, crystallises in golden-yellow leaflets, m. p. 130—131° (decomp.). 1-Phenyl-Δ^1-*cyclo*pentene-3-one in ethereal solution combines with mercuric chloride, forming the additive *product*, $C_{11}H_{10}O,HgCl_2$, obtained as large, colourless, transparent crystals, and with ferric chloride, yielding the additive *product*, $C_{11}H_{10}O,FeCl_3,OEt_2$, crystallising in ruby-red needles with a metallic lustre; both compounds are decomposed by water into their components. The *oxime*, $C_{11}H_{10}\!:\!NOH$, crystallises in white needles, m. p. 146—147°; the *semicarbazone*, $C_{11}H_{10}\!:\!N\cdot NH\cdot CO\cdot NH_2$, crystallises in small, white needles, m. p. 234° (decomp.); it may be obtained directly from phenacylacetone by acting on this compound with semicarbazide hydrochloride in the presence of sodium acetate. 1-Phenyl-Δ^1-*cyclo*pentene-3-one condenses with itself in alcoholic solution in the presence of a small quantity of sodium hydroxide, forming 5-*keto*-3 : 3′-*diphenyl*-$\Delta^{1(1'):3:2'}$-*bis*cyclo*pentenylidene*,  $\left.\begin{array}{l}CH—CO\\ CPh\cdot CH_2\end{array}\right\rangle C\!:\!C\left\langle\begin{array}{l}CH_2\cdot CH_2\\ CH=CPh\end{array}\right.$, dark yellow needles, m. p. 195—196°; the *hydrochloride*, $C_{22}H_{18}O,2HCl$, is a dark red substance. The ketone condenses also with benzaldehyde, yielding 1-*phenyl*-4-*benzylidene*-Δ^1-cyclo*pentene*-3-*one*,  $\left.\begin{array}{l}CH—CO\\ CPh\cdot CH_2\end{array}\right\rangle C\!:\!CHPh$, crystallising in light yellow scales, m. p. 186—187°, b. p. 260°/10 mm.; the *hydrochloride*, $C_{18}H_{14}O,2HCl$, is an orange-red, crystalline powder, m. p. 178°; the corresponding o-*hydroxybenzylidene* derivative, $C_{18}H_{14}O_2$, crystallises in brilliant, small, greenish-yellow prisms, m. p. 183—184°, and the p-*dimethylaminobenzylidene* derivative, $C_{20}H_{19}ON$ forms short, cinnamon-red prisms, m. p. 153—154°.

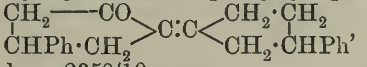
1-Phenyl-Δ^1-*cyclo*pentene-3-one, on reduction with zinc dust and aqueous potassium hydroxide, yields the *pinacone*,



$$\left.\begin{array}{l}CH_2\cdot CH_2\\ CPh=CH\end{array}\right\rangle C(OH)\cdot C(OH)\left\langle\begin{array}{l}CH_2\cdot CH_2\\ CH=CPh\end{array}\right.,$$

a yellowish-white, crystalline powder, m. p. about 235°; when reduced with sodium in wet ether, the unsaturated ketone is converted into 1-*phenyl*cyclo*pentane*-3-*ol*,  $\left.\begin{array}{l}CH_2—CH_2\\ CHPh\cdot CH_2\end{array}\right\rangle CH\cdot OH$, a colourless liquid,

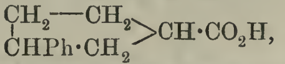
b. p. 155—156°/10 mm., which sets to a jelly when cooled in a freezing mixture; the *acetate*, $C_{11}H_{13}OAc$, is a colourless, viscid oil, b. p. 154°/12 mm.; the *phenylurethane*, $C_{11}H_{13}O\cdot CO\cdot NHPh$, crystallises in glistening leaflets, m. p. 99—100°. The alcohol is oxidised by chromic acid in glacial acetic acid to 1-*phenyl*cyclo*pentane*-3-*one*, $C_{11}H_{12}O$, a colourless liquid, b. p. 154—155°/10 mm.; the *semicarbazone*, $C_{12}H_{15}ON_3$, crystallises in white leaflets, m. p. 181° (decomp.). The ketone condenses with benzaldehyde in the presence of a small quantity of sodium hydroxide, forming 1-*phenyl*-2 : 4-*dibenzylidene*cyclo*pentane*-3-*one*, $C_{25}H_{20}O$, light yellow leaflets, m. p. 181°, and is converted by sodium ethoxide in alcohol into 4-*phenyl*cyclo*pentylidene*-1-*phenyl*cyclo*pentane*-3-*one*,

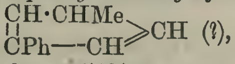


$$\begin{array}{l}CH_2\text{——}CO\\ CHPh\cdot CH_2\end{array}\!\!>C{:}C<\!\!\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CHPh\end{array},$$

a yellow, viscid oil, b. p. 235°/10 mm.

When heated with fuming hydrobromic acid in a sealed tube at 100°, 1-phenyl*cyclo*pentane-3-ol is converted into 3-*bromo*-1-*phenyl*cyclo*pentane*, $C_{11}H_{13}Br$, a colourless liquid, b. p. 139—140°/10 mm.; the latter compound reacts with magnesium, forming an additive *product*, which is decomposed by dilute sulphuric acid, yielding *phenyl*cyclo*pentane*, $C_{11}H_{14}$, a colourless, limpid oil, b. p. 213—215°/760 mm., D_{17}^{17} 0·958, n_D 1·5320. 3-Bromo-1-phenyl*cyclo*pentane, when treated with alcoholic potassium hydroxide solution, yields *phenyl*cyclo*pentene*, $C_{11}H_{12}$, a colourless, limpid liquid, b. p. 223—225°, D_{20}^{20} 0·965, n_D 1·5356; the product so obtained is probably a mixture of 1-phenyl-Δ^2-*cyclo*pentene and 1-phenyl-Δ^3-*cyclo*pentene. The same compound is formed on heating 1-phenyl*cyclo*pentane-3-ol with zinc chloride.

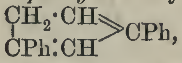
1-*Phenyl*cyclo*pentane*-3-*carboxylic acid*,  $\begin{array}{l}CH_2\text{—}CH_2\\ CHPh\cdot CH_2\end{array}\!\!>CH\cdot CO_2H$, is prepared by treating magnesium 3-bromo-1-phenyl*cyclo*pentane with carbon dioxide; it is a viscid, colourless oil, which solidifies to a vitreous mass in a freezing mixture; the *ammonium* salt, long, white needles, *calcium* salt, $C_{24}H_{26}O_4Ca$, white, silky needles, and *silver* salt, $C_{12}H_{13}O_2Ag$, were prepared. The product formed by the action of magnesium methyl iodide on 1-phenyl*cyclo*pentane-3-one is decomposed by dilute sulphuric acid, yielding 3-*phenyl*-1-*methyl*cyclo*pentadiene*,



$$\begin{array}{l}CH\cdot CHMe\\ CPh\text{—}CH\end{array}\!\!>CH\ (?),$$

large, colourless crystals, b. p. 151°/12 mm., m. p. 62°; it decomposes when exposed to the air, but is stable in an atmosphere of hydrogen; it is reduced by sodium in wet ether to 3-*phenyl*-1-*methyl*cyclo*pentane*, $C_{12}H_{16}$, a colourless liquid, b. p. 230—235°, D_{17}^{17} 0·950, n_D^{17} 1·5276. The following compounds are prepared in a similar manner: 3-*phenyl*-1-*ethyl*cyclo*pentadiene*, $C_{13}H_{14}$, b. p. 170—175°/12 mm., is obtained as a semi-solid mass at the ordinary temperature, which solidifies to white, silky needles at low temperatures; 3-*phenyl*-1-*ethyl*cyclo*pentane*, $C_{13}H_{18}$, is a colourless, limpid liquid, b. p. 270°,

D_{17}^{17} 0·948, n_D^{17} 1·5276 ; 1 : 3-*diphenyl*-$\Delta^{1:3}$-cyclo*pentadiene*,



$$\left.\begin{matrix}CH_2\cdot CH\\ | \\ CPh{:}CH\end{matrix}\right>CPh,$$

crystallises in yellowish-white needles, m. p. 156° ; its solutions exhibit a strong, blue fluorescence. W. H. G.

Preparation of Triphenylmethyl. JULIUS SCHMIDLIN (*Ber.*, 1908, **41**, 423—425).—The paper gives a detailed account of the apparatus and of the operations whereby triphenylmethyl can be obtained rapidly and conveniently in accordance with the equation $CPh_3\cdot MgCl + CPh_3Cl = 2CPh_3 + MgCl_2$. The apparatus can be used for the preparation of β-magnesium triphenylmethyl chloride, which crystallises in colourless prisms, carbonises on heating, forms a yellow solution in benzene, and reacts with oxygen even more rapidly than triphenylmethyl, yielding the peroxide and magnesium oxychloride.

C. S.

Structural Formula of Triphenylmethyl. JULIUS SCHMIDLIN (*Ber.*, 1908, **41**, 426—430).—Triphenylmethyl and α-magnesium triphenylmethyl chloride result when magnesium in moderate excess reacts gently with an ethereal solution of triphenylmethyl chloride in the presence of a moderate amount of iodine (Abstr., 1907, i, 26). With a large excess of iodine, the amount of triphenylmethyl is greatly diminished, and, if the reaction proceeds vigorously, a partial conversion of α-magnesium triphenylmethyl chloride into the β-isomeride occurs (Abstr., 1906, i, 392). Tschitschibabin employed the latter conditions in the experiments (Abstr., 1907, i, 1022), the results of which led him to doubt the existence of two isomeric magnesium triphenylmethyl chlorides. The author points out that Tschitschibabin's solution can have contained little or none of the α-isomeride, that his explanation of the formation of *p*-benzoyltriphenylmethane is impossible, and that its production from triphenylmethyl is negatived by the three following experiments. An ethereal solution of triphenylmethyl, free from the magnesium compound, does not react with benzaldehyde. Solid triphenylmethyl in benzene solution is equally non-reactive. The reaction between magnesium and triphenylmethyl chloride was so performed that the ethereal solution contained the triphenylmethyl, whilst the α-magnesium triphenylmethyl chloride was present exclusively in the precipitate; the solution did not react with benzaldehyde, whereas the precipitate yielded *p*-benzoyltriphenylmethane.

Tschitschibabin's argument that the so-called α- and β-magnesium triphenylmethyl chlorides react in the same way with benzoyl chloride and ethyl benzoate is countered by the statement that, under these conditions, the labile α-form changes into the stable β-isomeride.

C. S.

Various Cases of the Simultaneous Production of 1 : 6- and 2 : 7-Dimethylanthracenes. JAMES LAVAUX (*Compt. rend.*, 1908, **146**, 135—137. Compare Abstr., 1905, i, 43, 125, 640, 698 ; 1907, i, 25).—The author considers that *A*-dimethylanthracene, which gives a quinone, m. p. 169°, is the 1:6-isomeride. It is different from Louise's dimethylanthracene (*Ann. Chim. Phys.*, 1885, [vi], 6, 187), which forms a quinone, m. p. 170°, since a mixture of the quinones has a m. p. 15° lower. 1:6- and 2:7-Dimethylanthracenes, which have respectively m. p. 240° and m. p. 244·5°, form a curious mixture, apparently of a eutectic nature, which has the sharp m. p. 225°. This mixture is contained in the "dimethylanthracenes" obtained by Friedel and Crafts by the action of aluminium chloride on (1) xylyl chloride, (2) a mixture of methylene dichloride and toluene, and (3) benzyl chloride mixed with toluene, by Elbs and Wittich, and by Anschütz, using respectively chloroform and ethylene tetrabromide in place of methylene dichloride, and by Anschütz and Immendorff by the action of aluminium chloride on toluene, and also in the product isolated by Zincke and Waschendorff from coal tar. It cannot be separated into its components either by continued sublimation or fractional crystallisation; but repeated recrystallisation, carried out so that only a small portion of the dissolved solid separates, results in a gradual rise of the m. p. of the latter, and a small quantity of the 1:6-isomeride is thus obtained. The solid remaining in solution has m. p. 225°.

The mixture of quinones obtained on oxidation is, however, separable by alcohol, in which 1:6-dimethylanthraquinone is much more soluble than the 2:7-derivative. Reduction of the quinones thus separated gives the corresponding hydrocarbons. The author considers that the phenomenon of the formation of an eutectic mixture explains largely the confusion which exists in the literature on the subject. E. H.

Interaction of Aniline, Formaldehyde, and Sodium Hyposulphite. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 188837).—A mixture of methyleneaniline and sodium hyposulphite in water was shaken until the greater portion of the methylene compound had dissolved, and then treated rapidly with 30% formaldehyde and again shaken. The filtered solution was evaporated to dryness under reduced pressure, when a stable product was obtained, consisting of sodium anilinomethylsulphite,

$$NHPh\cdot CH_2\cdot O\cdot SO_2Na,$$

and sodium formaldehydesulphoxylate, $OH\cdot CH_2\cdot O\cdot SONa$. When the above conditions are employed, the unstable sodium anilinomethylsulphoxylate, $NHPh\cdot CH_2\cdot O\cdot SONa$, is not produced. G. T. M.

Action of Magnesium Organic Compounds on Hydramides. MAX BUSCH and LUDWIG LEEFHELM (*J. pr. Chem.*, 1908, [ii], 77, 1—20).—Busch and Rinck (Abstr., 1905, i, 519) showed that the action of magnesium alkyl haloids on Schiff's bases leads to the formation of *C*-alkylated primary bases. It was to be expected that the hydramides, $CHR\colon N\cdot CHR\cdot N\colon CHR$, which contain the typical grouping of Schiff's bases twice in the molecule, would yield in the same manner either monoalkylated, $CHR\colon N\cdot CHR\cdot NH\cdot CHR\cdot Alk$, or dialkylated, $CHR(NH\cdot CHR\cdot Alk)_2$, derivatives. It is found, however, that the magnesium alkyl haloid not only forms an additive compound with the unsaturated groupings, but also resolves a single carbon-nitrogen linking, this second action resembling the reduction of hydrobenzamide by sodium amalgam and alcohol to benzylamine and dibenzylamine. The reaction takes place according to two schemes: (I) $CHPh(N{:}CHPh)_2 + 3MgMeI \longrightarrow CHMePh\cdot N(MgI)_2 + CHMePh\cdot N(MgI)\cdot CHMePh \longrightarrow (+ 3H_2O) \longrightarrow CHMePh\cdot NH_2 + NH(CHMePh)_2 + 3Mg(OH)I$; (II) $CHPh(N{:}CHPh)_2 + 2MgMeI \longrightarrow CHPh[N(MgI)\cdot CHMePh]_2 \longrightarrow (+3H_2O) \longrightarrow CHO\cdot Ph + 2NH_2\cdot CHMePh + 2Mg(OH)I$. Hydrobenzamide enters into reaction with magnesium alphyl haloids according to both schemes, the proportions of primary and secondary bases formed varying with the alphyl haloid and the conditions, but with magnesium aryl haloids only according to scheme II. Anishydramide yields only primary amines, either with magnesium aryl or alphyl haloids. The behaviour of magnesium naphthyl bromide with hydrobenzamide is abnormal, in that considerable amounts of *iso*amarine are formed; this intramolecular change, which occurs with hydrobenzamide hydrochloride only at 240°, takes place here below 100°.

Di-a-phenylethylamine, $NH(CHMePh)_2$, is a viscid, yellow oil, which does not form a carbonate on exposure to air; the *hydrochloride*, $C_{16}H_{19}N,HCl$, sublimes unchanged above 240°; the *benzoyl* derivative, $C_{23}H_{23}ON$, white needles, m. p. 92°; the *phenylcarbamide*,

$$NHPh\cdot CO\cdot N(CHMePh)_2,$$

colourless prisms, m. p. 140°.

a-Phenylpropylamine hydrochloride, $CHEtPh\cdot NH_2,HCl$, crystallises in needles, m. p. 194°; the *benzoyl* derivative, $C_{16}H_{17}ON$, needles, m. p. 115—116°; the *phenylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CHEtPh$, needles or leaflets, m. p. 126—127°; the *benzenesulphonamide*,

$$SO_2Ph\cdot NH\cdot CHEtPh,$$

needles, m. p. 81°, is sparingly soluble in dilute sodium hydroxide.

Di-a-phenylpropylamine, $NH(CHEtPh)_2$, is a yellow oil, b. p. 293—294°/733 mm., and has an aromatic odour; the *hydrochloride*, $C_{18}H_{33}N,HCl$, long needles, m. p. 258°; the *benzoyl* derivative,

$$C_{25}H_{27}ON,$$

needles, m. p. 152°; the *benzenesulphonamide*, $C_{24}H_{27}O_2NS$, needles, m. p. 206°; the *nitrosoamine*, $C_{18}H_{22}N\cdot NO$, almost colourless needles, m. p. 74°, and gives Liebermann's reaction.

Benzoylphenylbutylamine, $C_{10}H_{14}NBz$, crystallises in white needles, m. p. 128°. *Di-a-phenylbutylamine*, $NH(CHPh\cdot C_3H_7)_2$, forms a viscid oil; the *hydrochloride*, $C_{20}H_{27}N,HCl$, crystallises in needles, m. p. 276°.

Tetraphenyldiethylamine, $NH(CHPh\cdot CH_2Ph)_2$, crystallises in soft needles, m. p. 99—100°, b. p. 266—268°/16 mm.; the *nitrosoamine*, $C_{28}H_{26}N\cdot NO$, white needles, m. p. 153—154°.

Benzhydrylamine nitrate crystallises in needles, m. p. 197°; the *sulphate*, m. p. 210°; the *benzoyl* derivative, $CHPh_2\cdot NHBz$, needles, m. p. 172°; the *benzenesulphonamide*, glistening needles, m. p. 182°.

a-Naphthylbenzylamine, $NH\cdot CHPh\cdot C_{10}H_7$, crystallises in needles, m. p. 121°, b. p. 255°/15 mm.; the *hydrochloride*, $C_{17}H_{15}N,HCl$, white needles, m. p. 275°, and, when treated with nitrite solution, yields phenylnaphthylcarbinol.

Benzoylisoamarine, $C_{21}H_{17}N_2Bz$, crystallises from alcohol in short needles, m. p. 288°.

The following substances are obtained from anishydramide.

a-Anisylethylamine, $NH_2\cdot CHMe\cdot C_6H_4\cdot OMe$, is a transparent oil, b. p. 127—131°/12 mm., has a characteristic odour, and forms a *carbonate* on exposure to air; the *hydrochloride*, $C_9H_{13}ON,HCl$, needles, m. p. 157°; the *nitrate*, $C_9H_{13}ON,HNO_3$, needles, m. p. 114°. a-*Phenyl*-b-*anisylethylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CHMe\cdot C_6H_4\cdot OMe$, leaflets, m. p. 125·5°.

a-Anisylpropylamine, $NH_2\cdot CHEt\cdot C_6H_4\cdot OMe$, is a transparent oil, b. p. 136—140°/12 mm.; the *hydrochloride*, $C_{10}H_{15}ON,HCl$, needles, m. p. 217—218°; the *nitrate*, leaflets, m. p. 176°; the *hydrogen sulphate*, $C_{10}H_{15}ON,H_2SO_4$, needles, m. p. 214°. The *benzoyl* derivative, $C_{10}H_{14}ONBz$, needles, m. p. 118°.

p-Methoxybenzhydrylamine, $NH_2\cdot CHPh\cdot C_6H_4\cdot OMe$ (Hantzsch and Kraft, Abstr., 1892, 338), b. p. 202—206°/12 mm.; the *nitrate*, leaflets, m. p. 164°; the *benzoyl* derivative, $C_{21}H_{19}O_2N$, needles, m. p. 174°. The hydrochloride, m. p. 194° (191°: Hantzsch and Kraft, *loc. cit.*), when treated with sodium nitrite, yields p-*methoxybenzhydrol*, $OH\cdot CHPh\cdot C_6H_4\cdot OMe$, which crystallises in white needles, m. p. 58°.

G. Y.

Action of Magnesium Organic Compounds on Benzylidene-alphylamines. Max Busch and Ludwig Leefhelm (*J. pr. Chem.*, 1908, [ii], 77, 20—24).—Busch and Rinck's method of preparing secondary bases by the action of magnesium organic compounds on Schiff's bases (Abstr., 1905, i, 519) is found to give good yields with benzylidene-methylamine and -ethylamine. The new secondary bases are colourless oils, which have an aromatic odour, distil unchanged, and form salts stable in aqueous solution.

a-Phenylethylmethylamine, $NHMe\cdot CHMePh$, from benzylidene-methylamine and magnesium methyl iodide, b. p. 87°/18 mm. or 184°/730 mm.; the *hydrochloride*, $C_9H_{14}NCl$, colourless needles, m. p. 173°. *a-Phenylpropylmethylamine*, $NHMe\cdot CHEtPh$, from benzylidenemethylamine and magnesium ethyl iodide, b. p. 96°/20 mm.; the *hydrochloride*, $C_{10}H_{15}N,HCl$, needles or prisms, m. p. 153°. *Methylbenzhydrylamine* (as-*diphenyldimethylamine*), $NHMe\cdot CHPh_2$, from benzylidenemethylamine and magnesium phenyl bromide, forms crystals, m. p. 40°, b. p. 168°/20 mm.; the *hydrochloride*, m. p. 238°; the *nitrate*, $C_{14}H_{15}N,HNO_3$, m. p. 146°.

a-Phenylethylethylamine, $NHEt\cdot CHMePh$, b. p. 90°/16 mm. or 194°/728 mm.; the *hydrochloride*, $C_{10}H_{15}N,HCl$, m. p. 201°. *a-Phenylpropylethylamine*, $NHEt\cdot CHEtPh$, b. p. 99°/20 mm. or 207—208°/729 mm.; the *hydrochloride*, m. p. 180°. *Ethylbenzhydrylamine*, $NHEt\cdot CHPh_2$, b. p. 175°/20 mm.; the *hydrochloride* becomes brown at 240°, m. p. 248°; the *nitrate*, m. p. 142°.

Di-a-phenylpropylamine (Busch and Leefhelm, preceding abstract) is prepared from benzylidenephenylpropylamine and magnesium ethyl iodide.

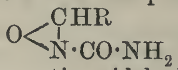
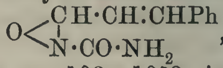
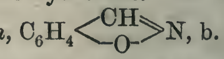
G. Y.

Benzylaminoacetal and Analogues. Leopold Rügheimer and P. Schön (*Ber.*, 1908, 41, 17—18).—A good yield of benzylaminoacetal is obtained by heating together benzylamine and chloroacetal at 130—140° (compare E. Fischer, Abstr., 1893, i, 300). Veratrylamine also reacts with chloroacetal at 100°.

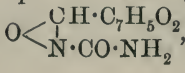
Veratrylamine (2 : 4-dimethoxybenzylamine) is best prepared by reducing methylvanillin oxime with zinc dust and acetic acid. The yield is 70%; there is also produced at the same time the secondary *amine*, $NH[CH_2\cdot C_6H_3(OMe)_2]_2$, b. p. above 250°/14 mm. (compare Juliusberg, Abstr., 1907, i, 219). W. R.

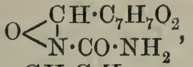
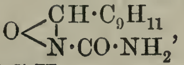
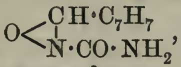
Dinitrodiphenylaminesulphonic Acids and their Transformation into Triphenylmethane Colouring Matters. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 186989).—1-Chloro-2 : 6-dinitrobenzene-4-sulphonic and 1-chloro-2 : 4-dinitrobenzene-6-sulphonic acids readily condense with metanilic acid in the presence of boiling aqueous sodium acetate to yield dinitrodiphenylaminesulphonic acids.

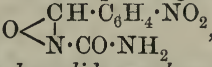
Potassium 2 : 6-*dinitrodiphenylamine*-4 : 3′-*disulphonate*,
$$SO_3K\cdot C_6H_2(NO_2)_2\cdot NH\cdot C_6H_4\cdot SO_3K,$$
produced in this way, crystallises from water in readily soluble, yellow, filamentous needles. When condensed in sulphuric acid with tetramethyldiaminobenzhydrol, this salt furnishes a leuco-derivative, which may be oxidised with manganic hydroxide to a triphenylmethane colouring matter. G. T. M.

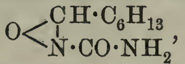
The Hydroxycarbamides and Carbamidoximes. II. A. CONDUCHÉ (*Ann. Chim. Phys.*, 1908, [viii], 13, 5—90. Compare this vol., i, 12).—The author has prepared a large series of carbamidoximes of the type  $O<\begin{matrix}CHR\\ N\cdot CO\cdot NH_2\end{matrix}$ by the condensation of *iso*hydroxycarbamide with aromatic aldehydes. Anisylidenecarbamidoxime, m. p. 133°. *Cinnamylidenecarbamidoxime*,  $O<\begin{matrix}CH\cdot CH{:}CHPh\\ N\cdot CO\cdot NH_2\end{matrix}$, m. p. 154—155°. Salicylidenecarbamidoxime, m. p. 102—105°, is very unstable, and decomposes in the light. Like the corresponding benzylidenecarbamidoxime (Abstr., 1905, i, 289; 1906, i, 593), all these compounds decompose on melting, yield the corresponding nitrile when treated with aqueous hydrochloric acid, or the hydrochloride of the corresponding acid amide when treated with alcoholic hydrogen chloride, the corresponding substituted carbamide when treated with reducing agents, and the corresponding oxime when treated with aqueous or alcoholic potassium hydroxide. In the case of salicylidenecarbamidoxime, the *indoxazen*,  $C_6H_4<\begin{matrix}CH\\ O\end{matrix}>N$, b. p. 86—87°/11 mm. or 90—92°/15 mm., is also formed in addition to the oxime by the action of aqueous potassium hydroxide, whilst with alcoholic potassium hydroxide it yields the nitrile.

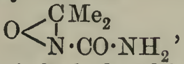
Anisylcarbamide has m. p. 160° (Goldschmidt and Polonowska give 167°).

Furfurylidenecarbamidoxime, m. p. 144—145° (Abstr., 1905, i, 289); *piperonylidenecarbamidoxime*,  $O<\begin{matrix}CH\cdot C_7H_5O_2\\ N\cdot CO\cdot NH_2\end{matrix}$, m. p. 156—157°;

vanillinylidenecarbamidoxime,  $\mathrm{O}<\begin{matrix}\mathrm{CH\cdot C_7H_7O_2}\\ |\\ \mathrm{N\cdot CO\cdot NH_2}\end{matrix}$, m. p. 134—135°; *cuminylidenecarbamidoxime,*  $\mathrm{O}<\begin{matrix}\mathrm{CH\cdot C_9H_{11}}\\ |\\ \mathrm{N\cdot CO\cdot NH_2}\end{matrix}$, m. p. 121—122°; p-*tolylidenecarbamidoxime,*  $\mathrm{O}<\begin{matrix}\mathrm{CH\cdot C_7H_7}\\ |\\ \mathrm{N\cdot CO\cdot NH_2}\end{matrix}$, m. p. 142—143°, are all well-defined, crystalline compounds.

When nitrated with fuming nitric acid in the presence of concentrated sulphuric acid at −15°, benzylidenecarbamidoxime yields a mixture of the three isomeric nitro-derivatives, in which the ortho- and meta-compounds preponderate; the same compounds can also be prepared directly from the corresponding nitrobenzaldehyde, o-*nitrobenzylidenecarbamidoxime,*  $\mathrm{O}<\begin{matrix}\mathrm{CH\cdot C_6H_4\cdot NO_2}\\ |\\ \mathrm{N\cdot CO\cdot NH_2}\end{matrix}$, m. p. 146—147°, forms yellow needles; m-*nitrobenzylidenecarbamidoxime,* m. p. 180°, forms yellow crystals, and p-*nitrobenzylidenecarbamidoxime,* m. p. 160°, forms plates.

With the exception of heptaldehyde, the aliphatic aldehydes do not yield carbamidoximes with *iso*hydroxycarbamide. *Heptylidenecarbamidoxime,*  $\mathrm{O}<\begin{matrix}\mathrm{CH\cdot C_6H_{13}}\\ |\\ \mathrm{N\cdot CO\cdot NH_2}\end{matrix}$, has m. p. 85—86°.

Acetone condenses with *iso*hydroxycarbamide to form *acetcarbamidoxime (dimethylcarbamidketoxime),*  $\mathrm{O}<\begin{matrix}\mathrm{CMe_2}\\ |\\ \mathrm{N\cdot CO\cdot NH_2}\end{matrix}$, which crystallises in massive prisms, m. p. 118—119°; is hydrolysed by hydrochloric acid forming the hydrochloride of hydroxycarbamide, mesityl oxide, and phorone; yields iso*propylcarbamide,* $\mathrm{CHMe_2\cdot NH\cdot CO\cdot NH_2}$, m. p. 154°, on reduction; acetoxime and potassium cyanate on treatment with potassium hydroxide, and benzylidenecarbamidoxime on boiling with benzaldehyde. Attempts to form corresponding carbamidoximes from methyl ethyl ketone or acetophenone were unsuccessful.

as-*Diphenylhydroxycarbamide,* $\mathrm{C_{13}H_{12}O_2N_2}$, decomp. 135°, prepared by the action of hydroxylamine hydrochloride on diphenylcarbamyl chloride, forms colourless needles; the hydrated *compound,*

$$\mathrm{C_{13}H_{12}O_2N_2,2H_2O},$$

forms massive, pale red crystals, which, when heated, decompose at 100°, solidify, and decompose again at 130°. It forms a *sodium* salt, $\mathrm{C_{13}H_{11}O_2N_2Na,H_2O}$, and does not yield condensation products with aromatic aldehydes or with ketones. With acetaldehyde, it forms the molecular *compound,* $\mathrm{C_{13}H_{12}O_2N_2,CH_3\cdot CHO}$, which is unstable in solution and decomposes at 129—130°; in view of all these facts, it is suggested that *as*-diphenylhydroxycarbamide has the constitution represented by the formula $\mathrm{OH\cdot C(NPh_2)\colon N\cdot OH}$, analogous to the hydroxycarbamide, m. p. 140° (this vol., i, 12).

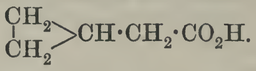
Hydroxyurethane does not condense with aromatic aldehydes, and probably has the constitution $\mathrm{OH\cdot C(OEt)\colon N\cdot OH}$.

Formamidoxime (*iso*uretine) reacts with benzaldehyde to form hydroxyphenylethenylamidoxime, $\mathrm{OH\cdot CHPh\cdot C(NH_2)\colon N\cdot OH}$, m. p. 163—164° (Tiemann, Abstr., 1884, 734, gives m. p. 140°).

M. A. W.

Molecular Refractions of some Carbamidoximes. A. Conduché (*Ann. Chim. Phys.*, 1908, [viii], 13, 91—95).—A determination of the molecular refractions of acetone, benzaldehyde, anisaldehyde, vanillin, piperonal and furfuraldehyde, and of the corresponding carbamidoximes (preceding abstract), show that the mean difference between the molecular refraction of the aldehyde and carbamidoxime is 13·06 for aliphatic, and 13·75 for aromatic, derivatives; the corresponding values calculated from Brühl and Conrady's values for the atomic refractions are 12·68 and 13·55 respectively.

M. A. W.

Some Transformations of *cyclo*Butanol. Nikolaus J. Demjanoff and M. Dojarenko (*Ber.*, 1908, **41**, 43—46. Compare Abstr., 1907, i, 605).—*cyclo*Butanol yields on oxidation with chromic acid, *cyclo*propanealdehyde and *cyclo*butanone; the semicarbazone of the former has m. p. 127—128°; the semicarbazone of the latter has m. p. 201° (compare Demjanoff, Abstr., 1907, i, 1023; Demjanoff and Fortunatoff, *ibid.*, 1032). *cyclo*Butanol yields on treatment with concentrated hydrobromic acid at 70° a monobromide; this compound has been described by W. H. Perkin (Trans., 1894, **65**, 950) as bromo*cyclo*butane; it is a liquid, b. p. 105—106°, n_D^{19} 1·476, D_{15}^{15} 1·4155, D_{23}^{23} 1·406, and is consequently very similar in its physical properties to the bromide obtained from *cyclo*propylcarbinol (Demjanoff and Fortunatoff, *loc. cit.*). In order to ascertain whether the *cyclo*butane compound had changed into a derivative of *cyclo*propane, the above bromide was converted into the magnesium compound, and treated with carbon dioxide. The *calcium* salt of the acid thus formed, $(C_5H_7O_2)_2Ca,2H_2O$, crystallises in glistening leaflets; the *silver* salt, $C_5H_7O_2Ag$, is likewise crystalline. It follows, therefore, that the acid is not *cyclo*butanecarboxylic acid, and since it does not correspond in properties with any known acid of the same composition it is probably cyclo*propylacetic acid*,  $\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>CH\cdot CH_2\cdot CO_2H$.

W. H. G.

Reaction between Phenols and Phosphorus Pentachloride. Wilhelm Autenrieth and Alfred Geyer (*Ber.*, 1908, **41**, 146—158).—An investigation on the course of the reaction between phosphorus pentachloride and phenols. When phenol, a cresol or β-naphthol (3 mols.) is treated with phosphorus pentachloride (1 mol.), the first product formed which can be isolated is a triarylphosphoryl dichloride, having the general formula $PCl_2(OR)_3$, where $R = Ph$, C_6H_4Me or $C_{10}H_7$. These compounds are identical with those prepared by Anschütz and Emery (Abstr., 1890, 34) by acting on esters of phosphorous acid, $P(OR)_3$, with chlorine, and are obtained as relatively stable, yellow or brown viscid oils, decomposing into hydrogen chloride and a chlorinated benzene derivative when heated at 200—300°. They react with aniline with the formation of a diaryl anilinophosphate and a substituted aniline, thus: $PCl_2(OR)_3 + 4NH_2Ph = NHPh\cdot PO(OR)_2 + NHRPh + 2NH_2Ph,HCl$.

These facts are not opposed to the views of Anschütz and Emery (*loc. cit.*), for it is quite probable that in the action of phosphorus pentachloride on phenol, the first compound formed is phenylphosphoryl tetrachloride, which then reacts with more phenol, thus: $PCl_4{\cdot}OPh + Ph{\cdot}OH \longrightarrow HCl + PCl_3(OPh)_2$; $PCl_3(OPh)_2 + Ph{\cdot}OH \longrightarrow PCl_2(OPh)_3$; at present, however, the only compound to be isolated has been the triarylphosphoryl dichloride.

Triphenylphosphoryl dichloride, prepared by the action of phosphorus pentachloride (1 mol.) on phenol (3 mols.), or by the method of Anschütz and Emery (*loc. cit.*), is stable below 180°, but decomposes fairly readily at 200—210° with the liberation of chlorobenzene. It reacts with aniline, yielding diphenyl anilinophosphate (compare Michaelis and Schulze, Abstr., 1894, i, 128, 588), diphenylamine, and aniline hydrochloride.

Tri-p-*tolylphosphoryl dichloride*, $PCl_2(O{\cdot}C_6H_4Me)_3$, prepared by heating *p*-cresol with phosphorus pentachloride at 140°, or by the action of chlorine on *p*-tolyl phosphite, is a yellow oil which decomposes at 200—210°, liberating *p*-chlorotoluene. It reacts with aniline, yielding the crystalline *di*-p-*tolyl anilinophosphate*,

$$NHPh{\cdot}PO(O{\cdot}C_6H_4Me)_2,$$

m. p. 125°. The following compounds were prepared by the same methods: *Tri*-m-*tolylphosphoryl dichloride* is a yellow oil decomposing at about 210°. *Di*-m-*tolyl anilinophosphate* crystallises in prisms, m. p. 87°. *Tri*-o-*tolylphosphoryl dichloride* is a yellowish-brown oil, decomposing at about 180°. *Di*-o-*tolyl anilinophosphate* crystallises in brilliant prisms, m. p. 126—127°. *Tri-β-naphthylphosphoryl dichloride* is a viscid, brown oil, decomposing above 310°. *Di-β-naphthyl anilinophosphate*, $C_{26}H_{20}O_3NP$, crystallises in glistening prisms and long needles, m. p. 193—195°. W. H. G.

Preparation of 5-Nitro-2-aminophenol-4-sulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 188378).—Carbonyl-2-aminophenol-4-sulphonic acid, obtained by passing carbonyl chloride into a cold solution of the basic sodium salt of 2-aminophenol-4-sulphonic acid, is nitrated to 5-*nitrocarbonyl*-2-*aminophenol*-4-*sulphonic acid* in a cold mixture of concentrated sulphuric and nitric acids, the product separating as the potassium salt on adding potassium chloride to an ice-cold aqueous solution of the sulphonation mixture. This salt is hydrolysed by warming at 90° with aqueous sodium hydroxide, and the solution, when acidified and cooled, deposits yellow crystals of 5-*nitro*-2-*aminophenol*-4-*sulphonic acid*; the diazo-derivative of the new acid is readily soluble. G. T. M.

2:3:4-Trinitrophenetole and some of its Derivatives. JAN J. BLANKSMA (*Rec. trav. chim.*, 1908, 27, 49—57).—Wender's dinitroaceto-*p*-phenetidine (Abstr., 1890, 751), contrary to that author's statement, is hydrolysed by boiling hydrochloric acid. Elimination of the amino-group from dinitro-*p*-phenetidine by diazotisation gives bright yellow leaflets, m. p. 101°, of 2:3-*dinitrophenetole*, $OEt{\cdot}C_6H_3(NO_2)_2$, of which the constitution is established by the formation of Bantlin's 2:3-dinitrophenol (Abstr., 1879, 237) when it is heated with hydrochloric acid in a sealed tube. On nitration, 2:3-dinitrophenetole gives a *trinitro-*

phenetole, $OEt{\cdot}C_6H_2(NO_2)_3$, in the form of colourless crystals, m. p. 117°. This cannot be 2 : 3 : 5-trinitrophenetole, which has m. p. 80° (Abstr., 1905, i, 431), and, since, by the action of alcoholic ammonia and subsequent removal of the amino-group by diazotisation it gives 2 : 4-dinitrophenetole, it must be 2 : 3 : 4-trinitrophenetole. The latter, when heated with alcoholic ammonia (1 mol.), is converted into 2 : 6-*dinitro-3-ethoxyaniline,* $OEt{\cdot}C_6H_2(NO_2)_2{\cdot}NH_2$, which forms yellow crystals, m. p. 130°; with excess of alcoholic ammonia, the product consists of a mixture of Barr's 2 : 4-dinitro-*m*-phenylenediamine (Abstr., 1888, 822) and dinitrophenetidine. Elimination of the amino-group from 2 : 6-dinitro-3-ethoxyaniline gives 2 : 4-dinitrophenetole, which, by the action of alcoholic ammonia, is transformed into 2 : 4-dinitroaniline. By the action of methylamine (2 mols.) on 2 : 3 : 4-trinitrophenetole, yellow leaflets of 2 : 6-*dinitro-3-ethoxymethylaniline,* $OEt{\cdot}C_6H_2(NO_2)_2{\cdot}NHMe$, m. p. 147°, are formed, which on nitration give colourless crystals of 2 : 4 : 6-trinitro-3-ethoxynitromethylaminobenzene, $OEt{\cdot}C_6H(NO_2)_3{\cdot}NMe{\cdot}NO_2$ (van Romburgh, Abstr., 1889, 1154). When heated in a sealed tube at 165° with alcoholic methylamine solution, 2 : 6-dinitro-3-ethoxymethylaniline gives 2 : 4-*dinitro*-m-*phenylenedimethyldiamine,* $C_6H_2(NO_2)_2(NHMe)_2$, in the form of yellow crystals, m. p. 170°, which are transformed by the action of nitric acid into van Romburgh's trinitro-*m*-phenylenedinitrodimethyldiamine (Abstr., 1888, 1185). 2 : 3 : 4-Trinitrophenetole reacts with an alcoholic solution of aniline, giving 2 : 6-*dinitro-3-ethoxydiphenylamine,* $NHPh{\cdot}C_6H_2(NO_2)_2{\cdot}OEt$, in the form of brilliant yellow crystals, m. p. 125°. By alcoholic sodium ethoxide solution, it is converted into 2 : 4-*dinitro*-1 : 3-*diethoxybenzene,* $C_6H_2(NO_2)_2(OEt)_2$, colourless crystals, m. p. 57°, which become ruby-red on exposure to sunlight, possibly owing to isomeric change (compare Hantzsch, Abstr., 1906, i, 352). The constitution of the dinitrodiethoxybenzene is established by its conversion into 2 : 4-dinitroresorcinol when hydrolysed with hydrochloric acid. 2 : 4-Dinitro-1 : 3-diethoxybenzene, on nitration, gives Stenhouse's 2 : 4 : 6-trinitro-1 : 3-diethoxybenzene (*Annalen*, 1867, **141**, 226). Sodium methoxide in methyl-alcoholic solution converts 2 : 3 : 4-trinitrophenetole into 2 : 6-*dinitro*-1-*methoxy*-3-*ethoxybenzene,* $OMe{\cdot}C_6H_2(NO_2)_2OEt$, which forms colourless crystals, m. p. 69°, becoming reddish-brown on exposure to sunlight. The latter substance, when dissolved in a mixture of nitric (D 1·52) and sulphuric acids, gives 2 : 4 : 6-*trinitro*-1-*methoxy*-3-*ethoxybenzene,* $OMe{\cdot}C_6H(NO_2)_3{\cdot}OEt$, in the form of colourless crystals, m. p. 92°, becoming red in the light. The constitution of this substance is fixed by its conversion by ammonia or methylamine into 2 : 4 : 6-trinitro-*m*-phenylenediamine or 2 : 4 : 6-trinitro-*m*-phenylenedimethylamine (van Romburgh, *loc. cit.*). By boiling with aqueous sodium carbonate solution for three hours, 2 : 3 : 4-trinitrophenetole is transformed into 2 : 4-*dinitro*-3-*hydroxyphenetole,* $OEt{\cdot}C_6H_2(NO_2)_2OH$, which forms bright yellow crystals, m. p. 118°, becoming red on exposure to light. E. H.

Action of Chlorodimethyl Ether on the Phenoxides of the Alkali Metals. ALBERT REYCHLER (*Bull. Soc. chim.*, 1907, [iv], 1, 1195—1198).—On diluting an alcoholic solution of hydroxydimethyl ether (prepared as described, this vol., i, 130) with benzene and passing in a current of hydrogen chloride, a solution of chlorodimethyl ether in benzene is obtained. With sodium phenoxide, this furnishes methylene phenylmethyl ether, $OPh\cdot CH_2\cdot OMe$ (compare Breslauer and Pictet, Abstr., 1907, i, 915), b. p. 189—190°, D_{15}^{15} 1·048, having an odour similar to that of phenetole. Methylene α-naphthyl methyl ether, prepared in an analogous manner, is an oily liquid, b. p. 296° (corr.), D_{15}^{15} 1·071, and is only volatilised by a current of steam. Methylene β-naphthyl methyl ether is a slightly yellow oily liquid, b. p. 301° (corr.), D_{15}^{15} 1·068. These three substances are insoluble in water, soluble in the usual organic solvents, are not attacked by alkaline liquids, but are decomposed by mineral acids, yielding variously coloured solids, similar to those produced by the action of formaldehyde on phenols (compare Baeyer, Abstr., 1873, 501, and Blumer, D.R.-P. 172877). When methyl salicylate reacts with chlorodimethyl ether in presence of alcohol containing a little sodium ethoxide, the *mixed ether*, $OMe\cdot CH_2\cdot O\cdot C_6H_4\cdot CO_2Me$, b. p. 156°/20 mm. and 284°(corr.)/atmospheric pressure, D_4^{17} 1·162, is formed. It is a colourless liquid, which resinifies when sulphuric acid is added to its solution in acetic acid or alcohol, and on hydrolysis by potassium hydroxide solution in alcohol furnishes the *potassium* salt of the methoxymethyl ether of salicylic acid, $OMe\cdot CH_2\cdot O\cdot C_6H_4\cdot CO_2K$, which is soluble in water, and is decomposed by dilute hydrochloric acid, yielding salicylic acid.

T. A. H.

Action of Chlorodimethyl Ether on Magnesium Phenyl Bromide. ALBERT REYCHLER (*Bull. Soc. chim.*, 1907, [iv], 1, 1198—1200).—Chlorodimethyl ether, prepared as already described (this vol., i, 130), does not react with magnesium in ether even in presence of a trace of iodine, and, like chloroform (Abstr., 1906, ii, 836), inhibits the reaction of magnesium with methyl iodide and ethyl bromide. It reacts vigorously with magnesium phenyl bromide in ether, furnishing, as a principal product, benzyl methyl ether.

Chlorodimethyl ether also reacts with magnesium bornyl chloride, prepared by Hesse's method (Abstr., 1906, i, 375), yielding, in addition to camphene, camphane, and other products, bornyl dimethyl ether, $C_{10}H_{17}\cdot CH_2\cdot OMe$, which was not isolated in a pure state. T. A. H.

Action of Potassium Persulphate on *p*-Cresol. T. KUMAGAI and RICHARD WOLFFENSTEIN (*Ber.*, 1908, 41, 297—300).—In the cases of toluene and *p*-toluonitrile, the interaction of persulphate leads to the formation of dibenzyl derivatives (Abstr., 1899, i, 424; 1901, i, 594). An extension of the research to *p*-cresol shows that the product obtained is dependent on the conditions of the experiment. In neutral solution, dihydroxydibenzyl is formed, but in acid solution, 2:5-dihydroxytoluene is the product obtained, the methyl group migrating during the change to an ortho-position (compare Bamberger, Abstr., 1895, i, 217). In alkaline persulphate solution, on the other hand, 3:4-dihydroxytoluene is formed [Chemische Fabrik auf Actien (vorm. Schering), D.R.-P. 81068, 81298]. W. R.

o-Vinylphenols. KARL FRIES and G. FICKEWIRTH (*Ber.*, 1907, 41, 367—373).—Contrary to Kunz-Krause's statement (Abstr., 1899, i, 200), the product obtained on distilling *o*-coumaric acid under the ordinary pressure is not *o*-vinylphenol, but a polymeride of this substance. It is found that the unimolecular *o*-vinylphenol may be prepared by heating *o*-coumaric acid under 15 mm. pressure. In the preparation of the homologues of vinylphenol, on the other hand, the corresponding coumaric acids may be distilled under the ordinary pressure. The vinylphenols are obtained as oils which gradually solidify, forming bimolecular, or more complicated, polymerides; the constitution of these is discussed. The unimolecular substances are again formed when the polymerides are heated at high temperatures.

o-*Vinylphenol* (o-*hydroxystyrene*), $OH\cdot C_6H_4\cdot CH:CH_2$, crystallises in needles, m. p. 29°, b. p. 108°/15 mm., decomp. on distillation under the ordinary pressure, forming a red and violet *resin*, yields o-*vinylphenoxyacetic acid*, $CH_2:CH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H$, m. p, 139°, when treated with bromoacetic acid in alkaline solution, and reacts with bromine in glacial acetic acid solution, forming 3 : 5-*dibromo-2-hydroxystyrene dibromide*, $OH\cdot C_6H_2Br_2\cdot CHBr\cdot CH_2Br$, which separates from light petroleum in small crystals, m. p. 105°, and behaves as a ψ-bromide, reacting with alkalis and alkali carbonates at the ordinary temperature. The dimolecular *o*-vinylphenol is insoluble in alkalis, does not form crystalline derivatives, and, on distillation under the ordinary pressure, decomposes in the same manner as the unimolecular substance.

2-*Hydroxy-α* : 4-*dimethylstyrene*, $OH\cdot C_6H_3Me\cdot CMe:CH_2$, b. p. 217°, is prepared from β : 4-dimethylcoumaric acid, and when heated, or more rapidly when boiled with hydrochloric acid, forms the *polymeride*, $(C_{10}H_{12}O)_2$; this is obtained as a white powder, m. p. 72—74°, b. p. 232°/15 mm., forms a crystalline, additive *compound* with ether, and is converted into the unimolecular phenol when distilled under the ordinary pressure. With bromine in glacial acetic acid solution, 2-hydro-α-4-dimethylstyrene forms hexabromothymol, m. p. 152° (148—149° : Baeyer and Seuffert. Abstr., 1901, i, 216), and on reduction with zinc dust in alkaline solution yields thymol.

6-*Hydroxy-α-3-dimethylstyrene*, $C_{10}H_{12}O$, b. p. 217°. The *benzoyl* derivative, $C_{17}H_{16}O_2$, crystallises in plates, m. p. 49°. The *polymeride*, $(C_{10}H_{12}O)_2$, does not form a crystalline additive compound with ether, and therefore could not be obtained free from the unimolecular phenol, into which it is transformed on distillation. These vinylphenols and their polymerides give red to reddish-brown colorations with concentrated sulphuric acid. G. Y.

Preparation of 5-Amino-α-naphthol-3-sulphonic Acid. LEOPOLD CASSELLA & CO. (D.R.-P. 188505).—α-Naphthylamine-5-sulphonic acid, when sulphonated with about 7 parts of fuming sulphuric acid (30% SO_3) first at 80° for eight and then at 120° for thirty hours, furnishes α-naphthylamine-2 : 5 : 7-trisulphonic acid, obtained by salting out in the form of its disodium salt; this compound on fusion with potassium hydroxide at 165—175° gives rise to 5-amino-α-naphthol-3:6-disulphonic acid, which, after acidifying the fused product, separates as the alkali hydrogen salt. 5-*Amino-a-naphthol-3-sulphonic acid* is obtained by heating the preceding disulphonate with 10% sulphuric acid at 130—135°. G. T. M.

Constitution of Iodoguaiacol. Eugène Tassilly and J. Leroide (*Bull. Soc. chim.*, 1908, [iv], 3, 124—126).—In a previous paper (Abstr., 1907, i, 515), the authors assigned the constitution

$$OH : OMe : I = 1 : 2 : 4$$

to an iodoguaiacol they prepared, and they now call attention to the fact that this constitution is incorrect in view of the work of Paul (Abstr., 1906, i, 843) and of Mameli (Abstr., 1908, i, 18).

T. A. H.

Separation of *o*- and *p*-Guaiacolsulphonic Acids. Chemische Fabrik von Heyden (D.R.-P. 188506).—The sulphonation of guaiacol is preferably carried out at 30—60°, and the product, when converted into normal calcium salt, is treated with calcium oxide ($\frac{1}{2}$ mol. CaO : 1 mol. guaiacol) or the corresponding amount of calcium chloride in ammoniacal solution. The solution of the basic salts rapidly deposits colourless, prismatic crystals of the basic calcium guaiacol-*p*-sulphonate; the basic salt of the ortho-sulphonate remains in solution. This separation may also be effected by means of the lead salts. A hot solution of the normal lead salts, when treated with lead acetate corresponding with $\frac{1}{2}$ mol. of PbO, gives a white precipitate, which at the boiling temperature contains only the basic para-sulphonate, the ortho-compound separating only on cooling. The patent gives a comparison of the properties of the potassium salts of *o*- and *p*-guaiacolsulphonic acid. The most striking differences are obtained with ammoniacal calcium or barium chloride, or with concentrated nitric acid. The former reagent gives a white precipitate with the para-salt, but no appreciable change with the ortho-isomeride. The latter reagent precipitates yellow dinitroguaiacol (m. p. 122°) from a 10% solution of the para-salt, but merely develops a dark red coloration with the ortho-salt. It is important that the guaiacol-*o*-sulphonic acid, employed therapeutically, should be quite free from the para-compound, as the latter has an unpleasant secondary reaction. G. T. M.

Successive Preparation of Mono- and Di-nitrosoresorcinols and of Resorubrin. Michele Barberio (*Gazzetta*, 1907, 37, ii, 577—585).—The author has determined the conditions of the reaction of nitrous acid with resorcinol which lead to the simultaneous formation of mono- and di-nitroresorcinols and of a colouring matter to which the name resorubrin is given.

The dinitrosoresorcinol obtained has the characters of the one prepared by Fitz (*Ber.*, 1875, 8, 631. Compare also Fèvre, Abstr., 1883, 733; Walker, Abstr., 1884, 1003; Henrich, Abstr., 1903, i, 88).

The mononitrosoresorcinol, $C_6H_3(OH)_2\cdot NO,2H_2O$, begins to turn brown at 130°, and deflagrates slightly at 134°; it seems to be isomeric with the compound prepared by Fèvre (*loc. cit.*).

Resorubrin is obtained as a dark green, amorphous substance, which, when rubbed, acquires a red colour with green fluorescence. It is a sensitive indicator, the violet colour imparted by it to a neutral aqueous solution being turned to blue by a trace of alkali, and to yellow by a trace of acid. In presence of ammonium salts, its sensitiveness is less marked, but is always greater than that exhibited by the other indicators. It dissolves in acetone or methyl, ethyl, or amyl alcohol, and, to a slight extent, in water or ether. Resorubrin behaves very similarly to diazoresorcinol in many ways, and also resembles lacmoid and resorcinol-blue in certain of its characters.

T. H. P.

Preparation of Dithymol: Action of Bromine on Dithymol. Henri Cousin and Henri Hérissey (*Compt. rend.*, 1908, **146**, 292—294. Compare this vol., i, 84; Dianine, Abstr., 1882, 623; Messinger and Vortmann, Abstr., 1889, 1150).—Dithymol is best prepared as follows. A solution of thymol (5 grams) in alcohol (50 c.c.) is poured into water (10 litres) at 50—60°, the liquid shaken, cooled, filtered, and the filtrate treated with (60 c.c.) ferric chloride solution (D 1·26). After three to four days, the precipitate is collected, dissolved in alkali, reprecipitated by acetic acid, and the crude dithymol so obtained purified by recrystallisation from 60% alcohol. The product is identical with Dianine's compound, except that it does not give an orange-yellow coloration with alkalis. Dithymol when brominated in chloroform solution gives *dibromodithymol*, $C_{20}H_{24}Br_2O_2$, which forms yellowish-white, prismatic crystals, m. p. 156—157° (corr.). Dibromodithymol is converted by bromine in chloroform solution into *dibromodithymoquinone* in the form of small, dark, garnet-red needles, m. p. 134° (corr. decomp.), which give an intense blue coloration with guaiacol.

E. H.

Action of Alcohols on Sodium Benzyloxide. Marcel Guerbet (*Compt. rend.*, 1908, **146**, 298—301).—It has been shown previously (Abstr., 1901, i, 182, 207; 1903, i, 3) that, when the primary aliphatic alcohols are heated at 220°—230° with their sodium derivatives, or the sodium compounds of other alcohols, condensation occurs, thus:

$$C_nH_{2n+1}\cdot OH + C_mH_{2m+1}\cdot ONa = C_{m+n}H_{2(m+n)+1}\cdot OH + NaOH,$$

the alcohol formed being partially converted by the sodium hydroxide into the corresponding acid with liberation of hydrogen. This reaction is now extended to the aromatic series. When benzyl alcohol is heated at 220—230° with sodium benzyloxide, not phenylbenzylcarbinol, $CH_2Ph\cdot CHPh\cdot OH$, but stilbene, dibenzyl, toluene, and benzoic acid are formed. Probably the stilbene and dibenzyl arise from the decomposition of phenylbenzylcarbinol formed at first, since Limpricht and Schwanert have shown (*Annalen*, 1870, **155**, 62) that this alcohol, when heated at 170° with alcoholic potash, loses water, forming stilbene. This change would probably be also effected by sodium benzyloxide, and part of the stilbene formed reduced by nascent hydrogen to dibenzyl. The toluene is probably formed by a reaction similar to the action of heat on benzyl alcohol and alcoholic potash (Cannizzaro *Annalen*, 1854, **92**, 114), and also by the reduction of dibenzyl. When sodium benzyloxide is heated with ethyl alcohol, benzyl alcohol and phenylpropyl alcohol, $CH_2Ph\cdot CH_2\cdot CH_2\cdot OH$, are formed. With *n*-propyl alcohol, an *alcohol*, $C_{10}H_{14}O$, b. p. 244—246°, probably having the constitution $CH_2Ph\cdot CHMe\cdot CH_2\cdot OH$, is produced. E. H.

Action of Organo-magnesium Derivatives on Ethylene Oxides. Ernest Fourneau and Marc Tiffeneau (*Bull. Soc. chim.*, 1907, [iv], 1, 1227—1233).—It had been shown previously by Jositsch (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 96; 1904, **36**, 6) that by the action of epichlorohydrin on ethyl magnesium bromide, a chloro-alcohol having the formula $CH_2Et\cdot CH(OH)\cdot CH_2Cl$ or $CH_2Cl\cdot CHEt\cdot CH_2\cdot OH$ is produced, but the authors after repeating this experiment have confirmed Kling's statement (*Bull. Soc. chim.*, 1904, **31**, 14) that only the chlorobromohydrin of glycerol is produced in this reaction. This substance is also obtained as a by-product in the following reactions. *Phenylchloro*iso*propyl alcohol*, $CH_2Ph\cdot CH(OH)\cdot CH_2Cl$, b. p. 153—154°/27 mm., 254—257°/760 mm., D_0^0 1·172, is obtained by treating magnesium phenyl bromide with epichlorohydrin in ether. It is converted by potassium hydroxide into allylbenzene oxide (Abstr., 1905, i, 591). With dry oxalic acid, it yields the *formyl* derivative, $CH_2Ph\cdot CH(O\cdot COH)\cdot CH_2Cl$, b. p. 250—245°(?), D_0^0 1·203, and with acetic anhydride the *acetyl* derivative, b. p. 147—148°/15 mm., D_0^0 1·162, and this, when warmed with lead acetate, gives the diacetin of benzylglycol, b. p. 163—166°/13 mm., 282—286°/760 mm., D_0^0 1·128. The parent chlorohydrin on oxidation with chromic acid yields a mixture of benzaldehyde, benzoic acid, chloroacetaldehyde, and chloroacetic acid. With cold nitric acid, *p*-nitrobenzoic acid is formed, and, on the first addition of nitric acid, spangles separate, probably of the nitric ester of the chlorohydrin, but this rapidly disappears. *Anisylchloro*iso*propyl alcohol*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$, b. p. 188—190°/24 mm., similarly obtained from magnesium *p*-anisyl bromide, yields, by treatment with potassium hydroxide, estragole oxide (Abstr., 1905, i, 591, this vol., i, 19), b. p. 149—151°/18 mm., D_0^0 1·109. *Benzylchloro*iso*propyl alcohol*, $CH_2Bz\cdot CH(OH)\cdot CH_2Cl$, b. p. 156°/22 mm., is similarly obtained from magnesium benzyl chloride.

All these chlorohydrins on treatment with dimethylamine yield amino-alcohols, identical with those obtained from the corresponding iodohydrins (Fourneau, Abstr., 1905, i, 57; Daufresne, this vol., i, 19), and, since in these two reactions the same amino-alcohols are produced, it follows that the constitution of the iodohydrins, formed by the action of iodine and yellow mercuric oxide on allylbenzene and on estragole, must be analogous to those of the chlorohydrins mentioned previously, since of the possible formulæ these alone account for the formation of the same amino-alcohols in the two cases. T. A. H.

Hexahydrotriphenylcarbinol [*cyclo*Hexyldiphenylcarbinol]. Julius Schmidlin and Robert von Escher (*Ber.*, 1908, **41**, 447—450).—*Hexahydrotriphenylcarbinol* (cyclo*hexyldiphenylcarbinol*), $C_6H_{11}\cdot CPh_2\cdot OH$, m. p. 71—72° (corr.), prepared from ethyl hexahydrobenzoate and magnesium phenyl iodide in ethereal solution, exhibits halochromy, dissolving in concentrated sulphuric acid to a yellow solution (compare Sabatier and Mailhe, Abstr., 1904, i, 809; Hell and Schaal, Abstr., 1907, i, 1049).

cyclo*Hexyl*-p-*dimethylaminophenylcarbinol*,

$$C_6H_{11}\cdot CH(OH)\cdot C_6H_4\cdot NMe_2,$$

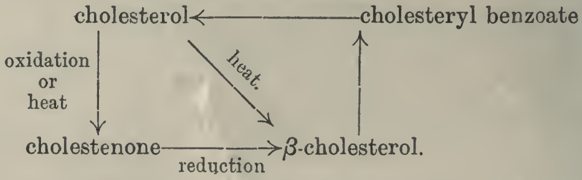
m. p. 86—87° (corr.), is prepared by the action of *p*-dimethylaminobenzaldehyde on magnesium *cyclo*hexyl bromide in ethereal solution.

C. S.

Cholesterol. V. Otto Diels and Karl Linn (*Ber.*, 1908, **41**, 260—266).—Although the ketone cholestenone differs markedly from cholesterol, the unsaturated, secondary alcohol from which it is derived, towards oxidising agents (Windaus, Abstr., 1906, i, 174), or towards reduction with sodium and amyl alcohol, the ketone giving rise to β-cholestanol and the alcohol to the α-cholestanol (Diels and Abderhalden, Abstr., 1906, i, 272), they both possess the same ring system, and are very closely related. This has been established by studying the behaviour of cholesterol when heated at 310—315°. The change does not occur with pure cholesterol, only occurring in the presence of a catalyst, such as an iron or zinc compound. During the change, hydrogen is evolved. On extraction of the mass with acetone and cooling, the isomeric β-*cholesterol* separates, and on recrystallisation forms white needles, m. p. 160°. It is probably a *cis-trans*-modification, as it is very similar to cholesterol in solubility, and forms dibromocholesterol on treatment with bromine; reduction with sodium and amyl alcohol gives α-cholestanol, and on benzoylation, cholesteryl benzoate is formed. From the acetone mother liquor cholestenone can be isolated.

If absolute alcohol is used in the reduction of cholestenone with sodium, β-cholesterol is obtained probably mixed with β-cholestanol.

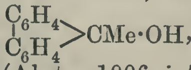
The relationships existing amongst these various compounds must be a very close one, as shown by the scheme:



A comparison of the m. p.'s and rotatory powers of cholesterol from biliary calculi, yolk of egg, and brain, gave 146·5, 147·5, and 148°, and $[\alpha]_D^{20}$ −24·92, −24·92, and −25·65°.

W. R.

Fluorene Series. Spontaneous Formation of an Ozonide. Maurice Daufresne (*Bull. Soc. chim.*, 1907, [iv], 1, 1233—1238).—9-Methylfluorene alcohol,



$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CMe\cdot OH,$$

prepared by Ullmann and Wurstemberger's method (Abstr., 1906, i, 76), when heated below its melting point, passes into a colourless *substance*, m. p. 330° (decomp.), which is insoluble in the usual organic solvents, and appears to be an ether. The alcohol on treatment with hydrochloric acid gives a colourless, amorphous substance, m. p. 160° (decomp.), which may be Manchot and Kriesche's diphenylene-ethylene (Abstr., 1905, i, 143). When dissolved in ether and treated with hydrogen chloride, the alcohol yields a crystalline *substance*, $C_{14}H_{12}O$, m. p. 85—86°, in which the oxygen atom is not present in a hydroxyl or carbonyl group. 9-Ethylfluorene alcohol, similarly prepared (*loc. cit.*), furnishes with aqueous or gaseous hydrogen chloride, diphenylenepropylene, $C_{15}H_{12}$ (*loc. cit.*), the *dibromide* of which melts at 94°. The hydrocarbon oxidises spontaneously in the air, forming an *ozonide*, $C_{15}H_{12}O_4$, which is colourless, amorphous, insoluble, and explodes at 160°. It decomposes spontaneously in air, evolving aldehyde and forming fluorenone. All the ozonides yet described (Harries, Abstr., 1904, i, 361) contain only three atoms of oxygen in place of four atoms as in this compound, and this appears to be the first instance of the spontaneous formation of an ozonide. T. A. H.

Mechanism of Transposition of Phenyl in Aromatic Iodohydrins MARC TIFFENEAU (*Bull. Soc. chim.*, 1907, [iv], 1, 1205—1220).—A theoretical paper, dealing with the changes accompanying the elimination from an aromatic iodohydrin of hydrogen and iodine from (1) the same carbon atom, and (2) from different carbon atoms.

The first case comprises iodohydrins derived from α-glycols by the substitution of an iodine atom for the stronger of the two alcohol functions, and includes the types $Ar{\cdot}CH(OH){\cdot}CH_2I$, $Ar{\cdot}C(OH)R{\cdot}CH_2I$, $Ar{\cdot}CH(OH){\cdot}CHI{\cdot}R$, and $Ar{\cdot}C(OH)R{\cdot}CHIR'$, in which the change proceeds according to the scheme

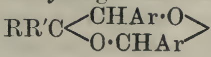
$$OH{\cdot}CArR{\cdot}C\boxed{HI}R' \longrightarrow OH{\cdot}CR{:}CArR' \longrightarrow COR{\cdot}CHR'Ar.$$

Until recently, this view has rested wholly on negative evidence (Abstr., 1907, i, 39), only the aldehydes or ketones forming the end products being known, but the intermediate products (homologues of vinyl alcohol) have recently been isolated in some cases, thus affording experimental proof of the accuracy of this view (Abstr., 1907, i, 922; this vol., i, 19).

When anethole, dissolved in methyl alcohol, is treated with iodine and yellow mercuric oxide, *anethole methyl iodohydrin*,

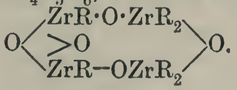
$$OMe{\cdot}C_6H_4{\cdot}CH(OMe){\cdot}CHMeI,$$

is formed; this, on treatment with potassium hydroxide in alcohol, yields α-methoxyanethole, and, when dissolved in ether and shaken with yellow mercuric oxide, gives the corresponding vinyl ether, $OMe{\cdot}C_6H_4{\cdot}CMe{:}CH{\cdot}OMe$, already described (*loc. cit.*). *iso*Safrole furnishes under analogous conditions a methyl iodohydrin, which is hydrolysed by potassium hydroxide in alcohol to form α-methoxy-*iso*safrole, b. p. 269°, and, on agitation with yellow mercuric oxide in ether, yields the *vinyl ether*, $CH_2O_2{:}C_6H_3{\cdot}CMe{:}CH{\cdot}OMe$, b. p. 280—282°, which is hydrolysed by dilute acids to the methylene ether of dihydroxyhydratropaldehyde, $CH_2O_2{:}C_6H_3{\cdot}CHMe{\cdot}CHO$.

The second case comprises iodohydrins derived from the α-glycols by the substitution of an iodine atom for the weaker alcohol function, and includes the types $Ar{\cdot}CHI{\cdot}CH(OH){\cdot}R$, $Ar{\cdot}CH(OH){\cdot}CRR'I$, and $R{\cdot}CH(OH){\cdot}CArR'I$, which behave like the glycols (Abstr., 1906, i, 662, 724, 965; 1907, i, 130, 404; Faworsky, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 741), probably forming first, by the elimination of hydrogen and iodine, diethylenic oxides, $2Ar\cdot CH(OH)\cdot CRR'I \rightarrow$  $RR'C{<}\begin{smallmatrix}CHAr\cdot O\\ O\cdot CHAr\end{smallmatrix}{>}CRR'$, which undergo asymmetrical fission, forming unstable, intermediate compounds of the type $-CRR'\cdot CR''R'''\cdot O-$, that in turn undergo transformation in various ways, depending on the position and nature of the substituent groups, forming ultimately aldehydes or ketones. T. A. H.

Mechanism of the Transposition of Phenyl in Iodohydrins and Aromatic Glycols. MARC TIFFENEAU (*Compt. rend.*, 1908, **146**, 29—32).—The author has put forward the view (Abstr., 1907, i, 404) that only (1) the α-glycols, α-chlorohydrins, and tetra-substituted ethylene oxides, and (2) the poly-substituted aromatic glycols of the general formulæ $OH\cdot CHAr\cdot CRR'\cdot OH$ and $OH\cdot CHAr\cdot CHAr'\cdot OH$, and the aromatic halohydrins of the general formulæ $OH\cdot CRAr\cdot CHXR'$ and $OH\cdot CHAr\cdot CRR'X$, are capable of undergoing intramolecular change when transformed into aldehydes or ketones, not as Houben and Führer (this vol., i, 73) have assumed, that these compounds always undergo such change. The author has previously emphasised the fact that the molecular transpositions are conditioned by the nature of the reagent employed (Abstr., 1907, i, 39), some reagents (HgO, $AgNO_3$, Ag_2O) effecting the migration of the aromatic radicle, whilst others (alcoholic potash and the alkali ethoxides) withdraw a molecule of hydracid without producing intramolecular change (Abstr., 1907, i, 922, this vol., i, 19). ααβ-Triphenylethane-αβ-diol, when heated with sulphuric acid, gives, not triphenylacetaldehyde, but a compound, $C_{20}H_{16}O$, m. p. 136°, identical with Biltz's triphenylvinyl alcohol (Abstr., 1899, i, 439). E. H.

Glucinum and Zirconium Benzoates. SEBASTIAN M. TANATAR and E. K. KUROVSKI (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1630—1632. Compare Abstr., 1907, i, 888).—Glucinum benzoate is formed by the action of an aqueous solution of sodium benzoate on an acid solution of glucinum acetate. It is a white, amorphous substance, similar in properties to compounds of the type Gl_4OR_6, and yields non-conducting solutions in benzene and acetone. Its structural formula is probably $R_3Gl\cdot O\cdot GlR_2\cdot[OGlR_2]\cdot_7OGlR_3$ (where $R = C_7H_5O_2$). The zirconium salt, $Zr_4O_5R_6$, is similar to the glucinum salt, and can be represented thus:



$$O\left\langle\begin{matrix}ZrR\cdot O\cdot ZrR_2\\ >O\\ ZrR-OZrR_2\end{matrix}\right\rangle O.$$

Z. K.

Esterification of Benzoic Acid. ISAAC K. PHELPS, M. A. PHELPS, and R. W. OSBORNE (*Amer. J. Sci.*, 1908, [iv], **25**, 39—48. Compare Abstr., 1907, i, 823; Fischer and Speier, Abstr., 1896, i, 201; Taylor, Abstr., 1905, i, 852).—The method described previously for the preparation of ethyl succinate has been applied to the preparation of ethyl benzoate. The amount obtained varies with the proportion of alcohol and hydrochloric acid used, and is increased by the addition of fused zinc chloride. By passing the vapour of 400 c.c. of absolute alcohol, containing 5 grams of hydrogen chloride, into 50 grams of benzoic acid and 10 grams of zinc chloride maintained at 100—110° for four hours, the theoretical yield of ester was obtained. Complete esterification could also be attained by treating 50 grams of benzoic acid and 2 grams of sulphuric acid with 200 c.c. of absolute alcohol.

R. J. C.

Preparation of Benzoylalkylamino-alcohols. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 187209).—The benzoyl derivatives of the alkylamino-alcohols, which have valuable anæsthetic properties, can be prepared by heating the alkyl benzoates with an alkylamino-alcohol.

β-Diethylaminoethyl benzoate, $Ph\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$, a colourless oil, b. p. 132°/5 mm., prepared by heating together methyl benzoate and β-diethylaminoethyl alcohol, when treated with alcoholic hydrogen chloride, yields a soluble *hydrochloride*, needles, m. p. 124°.

β-Dimethylaminoethyl benzoate, $Ph\cdot CO_2\cdot CH_2\cdot CH_2\cdot NMe_2$, uncrystallisable oil; *hydrochloride*, lustrous needles, m. p. 148°, was obtained by heating phenyl benzoate and β-dimethylaminoethyl alcohol at 170—180°.

β-Diamylaminoethyl benzoate, $Ph\cdot CO_2\cdot CH_2\cdot CH_2\cdot N(C_5H_{11})_2$, an oil obtained from ethyl benzoate and β-diamylaminoethyl alcohol at 190°, furnishes a *hydrochloride*, needles, m. p. 107—108°, and soluble in water, alcohol acetone, and ethyl acetate, and an acid *oxalate*, m. p. 158°, soluble in dilute alcohol.

*Diethylamino*iso*propyl benzoate*, $Ph\cdot CO_2\cdot CHMe\cdot CH_2\cdot NEt_2$, an uncrystallisable oil obtained from methyl benzoate and diethylamino*iso*propyl alcohol, gives rise to a very soluble *hydrochloride* and *oxalate*, and a *picrate*, crystallising from dilute alcohol in yellow spicules.

G. T. M.

Nitration of Methyl 3-Nitro-4-dimethylaminobenzoate. Frédéric Reverdin and A. de Luc (*Bull. Soc. chim.*, 1908, [iv], 3, 126—133; *Ber.*, 1908, **41**, 501—502; *Arch. Sci. phys. nat.*, 1908, 25, 133—145).—In attempting to nitrate 3-nitro-4-dimethylaminobenzoic acid (Abstr., 1907, i, 620), a small quantity of a substance was obtained which was believed to be a polynitro-derivative of the acid, but has since been found to be a mixture of products, and further experiments have shown that it is impossible to obtain polynitro-derivatives of this acid.

Methyl 3-nitro-4-dimethylaminobenzoate (Abstr., 1906, i, 273), when treated with nitric acid (D 1·52) in presence of acetic acid, yields *methyl* 3 : 5-*dinitro*-4-*nitrosomethylaminobenzoate*, m. p. 88°, which crystallises in leaflets from dilute alcohol or acetic acid, or a mixture of benzene with light petroleum. It gives Liebermann's reaction, and its solution in alcohol gives with solution of sodium hydroxide a reddish-violet colour. When boiled with mineral acids, it yields 3 : 5-*dinitro*-4-*methylaminobenzoic acid*, m. p. 223—224°, which crystallises in lemon-yellow, prismatic needles, and is coloured reddish-brown by sodium hydroxide in alcohol. *Methyl* 3 : 5-*dinitro*-4-*methylaminobenzoate*, m. p. 123—124°, obtained as a by-product in the same reaction, or when the parent ester is heated with phenol, crystallises in orange-yellow spangles.

When boiled with sodium carbonate solution, or when merely moistened with sodium hydroxide solution in alcohol and set aside, methyl 3 : 5-dinitro-4-nitrosomethylaminobenzoate furnishes, first, 3 : 5-dinitro-4-methylaminobenzoic acid and, finally, 3 : *5-dinitro-4-hydroxybenzoic acid*, m. p. about 245°, which forms yellow needles from acetic acid.

When methyl 3-nitro-4-dimethylaminobenzoate is treated with nitric acid in presence of sulphuric acid at 16°, *methyl* 3 : 5-*dinitro*-4-*nitromethylaminobenzoate*. m. p. 126°, crystallising in almost white, nacreous spangles from a mixture of benzene and light petroleum, is formed, together with some 3-nitro-4-methylaminobenzoic acid. The first of these products gives a fine reddish-violet colour with sodium hydroxide in alcohol, and when boiled with dilute hydrochloric acid or with sodium carbonate solution is, in part, converted into the free *acid*, m. p. 200°, which crystallises in lemon-yellow spangles.

When nitric acid (D 1·52) is added to the parent ester, dissolved in sulphuric acid, and the temperature raised to 35—40°, *methyl* 3-*nitro*-4-*methylaminobenzoate*, m. p. 145°, crystallising in lemon-yellow prisms from a mixture of benzene and light petroleum, is formed.

If the nitration is effected with nitric acid (D 1·52) alone at −2° to 4°, methyl 3 : 5-dinitro-4-nitromethylaminobenzoate is formed, whereas with acid of D 1·2—1·4, at the ordinary temperature, or on warming for a short time at 100°, methyl 3 : 5-dinitro-4nitrosomethylaminobenzoate is produced. T. A. H.

Addition of Halogens to Cinnamic Acid and Some of its Derivatives. ARTHUR MICHAEL and HOWARD D. SMITH (*Amer. Chem. J.*, 1908, **39**, 16—28).—It has been shown previously (Abstr., 1896, i, 130, 133) that in the case of stereoisomeric dibasic acids, the application of the addition-elimination principle provides a means of expressing the relationship between their physical and chemical properties. Thus, of two such stereoisomerides, the unstable maleinoid form should have a lower m. p. and a greater solubility than the fumaroid form. The stereoisomeride of higher m. p. is the form which is produced by the addition of hydrogen halide or halogen to the corresponding acetylenecarboxylic acid, and also loses the added atoms more easily with regeneration of the original acid.

These generalisations were applicable to the cinnamic acids until Liebermann and Finkenbeiner (Abstr., 1905, i, 663) observed that, when cinnamic acid is treated with chlorine in the dark, a dichloride is produced of m. p. 86° instead of the stereoisomeric form, of m. p. 168°. From this, it would appear as if the dichloride of higher m. p. were the primary addition product of *allo*cinnamic acid instead of that of cinnamic acid. On the other hand, it has been shown by Liebermann (Abstr., 1891, 832; 1896, i, 526) that both *allo*cinnamic acid and its methyl ester react in the dark with excess of bromine, with formation of 30—40% of a dibromide of lower m. p., together with the ordinary form, and that the products of lower m. p. are not obtained from cinnamic acid and its ester under the same conditions.

It is now found that when a cold solution of cinnamic acid and chlorine in carbon tetrachloride is exposed to direct sunlight, the chloride of higher m. p. is formed together with a relatively small amount of the stereoisomeride, but that a much larger proportion of the latter form is produced if the light is passed through solutions capable of absorbing the ultra-violet rays. It is therefore concluded that the conversion of the *allo*dichloride into the ordinary form is due to absorption of energy from the actinic rays. It has also been observed that a considerable quantity of the *allo*-form is produced if the reaction takes place in diffused light. Methyl cinnamate and cinnamyl chloride behave in a similar manner. *allo*Cinnamic acid, however, yields the dichloride of higher m. p. as the primary additive product together with a small quantity of an oily dichloride which may be the dichloride of lower m. p. It is considered, however, that the latter compound is probably formed from some cinnamic acid produced by the transformation of *allo*cinnamic acid by the action of the halogen.

Experiments on the action of bromine on methyl and ethyl cinnamates have shown that, under the conditions in which a quantitative yield of the *allo*dichloride is obtained, only a small quantity of the *allo*dibromide is produced, and that the yield of this substance depends largely on the solvent employed. It is evident that these additive reactions are governed by subtle conditions, which vary with the reagent to an extent quite unknown in other groups of unsaturated acids. These results confirm those of Michael and Whitehorne (Abstr., 1902, i, 32), but do not agree with those of Sudborough and Thompson (Trans., 1903, 83, 671), who were unable to obtain more than a trace of ethyl cinnamate *allo*dibromide. E. G.

Preparation of Alkylaminoalkyl Aminocinnamates. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 187593).—The alkylaminoalkyl esters of the aminocinnamic acids may be prepared by the following methods: (1) Reduction of an alkylaminoalkyl nitrocinnamate, (2) alkylation of the aminocinnamic acids with an alkylaminocarbinol in the presence of hydrochloric or sulphuric acid, and (3) warming together an alkylaminocarbinol and an alkylaminocinnamate.

These new alkylamino-esters are valuable anæsthetics, greatly surpassing in this respect the alkylaminoalkyl benzoates.

β-Diethylaminoethyl p-*nitrocinnamate*,

$$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2\cdot CH_2\cdot CH_2NEt_2,$$

reddish-yellow crystals, m. p. 44°, prepared by condensing *p*-nitrocinnamyl chloride with *β*-diethylaminoethyl alcohol on reduction with tin and hydrochloric acid, yields *β-diethylaminoethyl* p-*aminocinnamate*, $NH_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$, pale yellow spicules, m. p. 89°.

The patent contains references to seven other alkylamino-esters derived from the three aminocinnamic acids. G. T. M.

β-Alkylcinnamic Acids. III. GEORG SCHROETER [with OTTO BUCHHOLZ] (*Ber.*, 1908, 41, 5—12. Compare Abstr., 1904, i, 415; 1907, i, 530).—A 90% yield of *β*-methylcinnamic acid from acetophenone and ethyl bromoacetate is considered to be unattainable and incorrect (compare Rupe and Busolt, this vol., i, 23). In the case of substituted β-methylcinnamic acids where the substitution occurs in the nucleus, the yields obtained are similar to that of β-methylcinnamic acid itself. The yields of side-chain homologues, however, are almost quantitative.

p-*Methoxy-β-methylcinnamic acid*, $OMe\cdot C_6H_4\cdot CMe\colon CH\cdot CO_2H$, m. p. 156·5°, obtained from *p*-methoxyacetophenone, ethyl iodoacetate, magnesium, and benzene, heating the crude ethyl anisylmethylhydracrylate formed, first at 100—120° and then at 150°, distilling, and subsequently hydrolysing the ester, crystallises from alcohol. Should the hydracrylic ester be distilled, it is decomposed into ethyl acetate and methoxyacetophenone:

$$OMe\cdot C_6H_4\cdot CMe(OH)\cdot CH_2\cdot CO_2Et = OMe\cdot C_6H_4\cdot COMe + CH_3\cdot CO_2Et.$$

The corresponding p-*ethoxy*-derivative, $OEt\cdot C_6H_4\cdot CMe\colon CH\cdot CO_2H$, separates from carbon disulphide or alcohol in well-formed crystals, and also forms a liquid, crystalline phase (compare Vorländer, Abstr., 1907, ii, 70, 337), m. p., I, 122·2—122·8°, m. p. II, 159·2—159·4°; *p*-β-dimethylcinnamic acid forms two solid phases and one liquid crystalline phase.

*β-Phenyl-β-*n*-propylhydracrylic acid*, $OH\cdot CPrPh\cdot CH_2\cdot CO_2H$, obtained when the crude ester is hydrolysed first and distilled afterwards, separates from benzene in crystals, m. p. 121·5—122°; its *silver* salt, $C_{12}H_{15}O_3Ag$, is white. When the hydracrylic acid is dissolved in sulphuric acid and ice added, solid β-*n*-propylcinnamic acid is obtained (Abstr., 1907, i, 531). If, however, the crude hydracrylic ester is distilled and subsequently hydrolysed, a mixture of two possibly stereoisomeric propylcinnamic acids results.

*β-Phenyl-β-*n*-butylhydracrylic acid*, $OH\cdot CPh(C_4H_9)\cdot CH_2\cdot CO_2H$, from *n*-valerophenone, crystallises from carbon disulphide, m. p. 106—107°, and gives *β-*n*-butylcinnamic acid*, $CPh(C_4H_9)\colon CH_2\cdot CO_2H$, which crystallises from petroleum, m. p. 48—49°, on solution in sulphuric acid.

The β-ethyl-, β-*n*-propyl-, and β-*n*-butyl-phenylhydracrylic acids were compared as regards their stability, by heating the acids in tubes connected with flasks containing baryta water. The *n*-propyl acid gave a regular stream of carbon dioxide at 135°, the *n*-butyl at 145°, and the ethyl at 150°. The quantities of carbon dioxide evolved, after heating for thirty minutes at that temperature, were approximately ethyl : propyl : butyl = 2 : 5 : 3. W. R.

Triphenylacetic and Tritolylacetic Acids. JULIUS SCHMIDLIN and HERBERT H. HODGSON (*Ber.*, 1908, 41, 438—447).—The authors use the theory advanced by Werner to explain the mobility of the atom or group attached to the triphenylmethyl complex in triphenylmethane derivatives (Abstr., 1906, i, 436), to account for the stability of the halogen in triphenylacetyl chloride. By the theory, the carbonyl group must have a residual affinity which, exerted on the halogen atom, endows the latter with its exceptional stability. The theory is extended to include the cases of picryl chloride and *s*-trinitrobenzoyl chloride, the halogen atom in the former being, as is well known, very easily displaced, whilst the latter is affected only slightly by boiling water (compare V. Meyer, Abstr., 1895, i, 91).

Triphenylacetyl chloride, $CPh_3\cdot COCl$, prepared by Fischer's method (Abstr., 1905, i, 263), separates from benzene in colourless needles or prisms, m. p. 116—118° (decomp.), but after repeated crystallisation the m. p. rises to 128° (decomp.), carbon monoxide being evolved in both cases. The acid chloride is unaffected by moist air, can be crystallised from alcohol, and is only slowly attacked by hot 10% potassium hydroxide. It yields the following esters after being heated for eight hours with the corresponding alcohol: *methyl* ester, m. p. 186° (corr.), distils without decomposition, but after prolonged heating at the b. p. loses carbon dioxide; *ethyl* ester, m. p. 120—121° (corr.), distils unchanged, but after twenty minutes' heating at the b. p. loses carbon dioxide and ethylene, and yields triphenylmethane; iso*amyl* ester, m. p. 78·5—79·5° (corr.). The *phenyl* ester, obtained from the acid chloride and phenol after four hours on the water bath, has m. p. 124·5—125° (corr.), and carbonises on distillation.

Triphenylacetyl chloride reacts in benzene with dry ammonia to form triphenylacetamide, m. p. 246—247° (corr.) (E. and O. Fischer give m. p. 210°), and with aniline to form *triphenylacetanilide*,

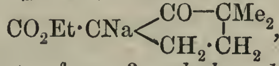
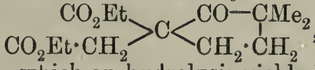
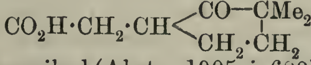
$$CPh_3\cdot CO\cdot NHPh,$$

m. p. 173·5—174·5° (corr.).

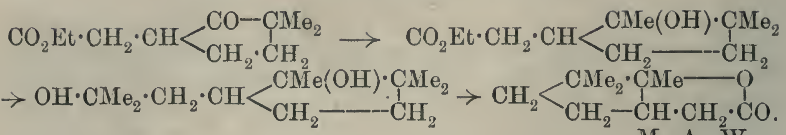
p-*Tritolylacetic acid*, $C(C_7H_7)_3\cdot CO_2H$, m. p. 226—228° (corr.), is ultimately obtained when carbon dioxide is passed into an ethereal solution of magnesium *p*-tritolylmethyl chloride at the time of its formation. It loses carbon dioxide above 250°. C. S.

Syntheses in the Camphor Series. Complete Synthesis of β-Campholenolactone.

GUSTAVE BLANC (*Compt. rend.*, 1908, **146**, 77—79).—The author has synthesised β-campholenolactone from αα-dimethyladipic acid through a similar series of reactions to those whereby the lactone of 1 : 3-dimethyl*cyclo*pentane-3-ol-4-acetic acid was obtained from β-methyladipic acid (this vol. i, 20).

Ethyl αα-dimethyladipate, b. p. 148°/18 mm., when treated with sodium, yields a sodium *derivative*,  $CO_2Et\cdot CNa<\begin{matrix}CO-CMe_2\\ \vert\\ CH_2\cdot CH_2\end{matrix}$, which condenses with ethyl bromoacetate to form 3-*carbethoxy*-1 : 1-*dimethyl*cyclo*pentane-2-one-3-acetic acid*,  $\begin{matrix}CO_2Et\\ CO_2Et\cdot CH_2\end{matrix}>C<\begin{matrix}CO-CMe_2\\ \vert\\ CH_2\cdot CH_2\end{matrix}$, a colourless, oily liquid, b. p. 165°/12 mm., which on hydrolysis yields 1 : 1-*dimethyl*cyclo*pentane-2-one-3-acetic acid*,  $CO_2H\cdot CH_2\cdot CH<\begin{matrix}CO-CMe_2\\ \vert\\ CH_2\cdot CH_2\end{matrix}$, m. p. 85°, identical with the acid already described (Abstr., 1905, i, 680); it forms an *oxime*, m. p. 160°, a semicarbazone, m. p. 210°, and is reduced by sodium and alcohol to form 1 : 1-*dimethyl*cyclo*pentane-2-ol-3-acetic acid*, $C_9H_{16}O_3$, m. p. 109—110°, together with a small quantity of the lactone, $C_9H_{14}O_2$.

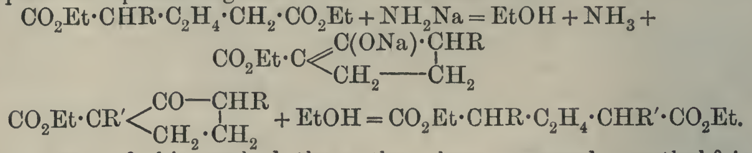
The *methyl* ester of the ketonic acid has b. p. 120°/14 mm.; the *ethyl* ester, b. p. 129°/13 mm., is converted by the action of magnesium methyl iodide and subsequent hydrolysis into a *glycol*, b. p. 130°/15 mm., which yields β-campholenolactone when treated with acids; the following scheme represents the last three stages of the synthesis:



$$CO_2Et\cdot CH_2\cdot CH<\begin{matrix}CO-CMe_2\\ CH_2\cdot CH_2\end{matrix} \rightarrow CO_2Et\cdot CH_2\cdot CH<\begin{matrix}CMe(OH)\cdot CMe_2\\ CH_2 - CH_2\end{matrix}$$
$$\rightarrow OH\cdot CMe_2\cdot CH_2\cdot CH<\begin{matrix}CMe(OH)\cdot CMe_2\\ CH_2 - CH_2\end{matrix} \rightarrow CH_2<\begin{matrix}CMe_2\cdot CMe - O\\ CH_2-CH\cdot CH_2\cdot CO.\end{matrix}$$

M. A. W.

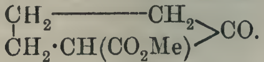
Synthesis of Racemic Dihydrocamphoric Acid. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1908, **146**, 82—84).—When the esters of α-alkyladipates (Abstr., 1900, i, 171) are treated with sodamide, then corresponding ester of 3-alkyl-2-*cyclo*pentanonecarboxylic acid is formed, and the 1 : 3-dialkyl substituted derivative of this acid by the action of sodium ethoxide at 140—150° yields the corresponding ester of α : δ-dialkyladipic acid, the following equations representing the course of the reactions :



$$CO_2Et\cdot CHR\cdot C_2H_4\cdot CH_2\cdot CO_2Et + NH_2Na = EtOH + NH_3 + CO_2Et\cdot C<\begin{matrix}C(ONa)\cdot CHR\\ CH_2 - CH_2\end{matrix}$$
$$CO_2Et\cdot CR'<\begin{matrix}CO-CHR\\ CH_2\cdot CH_2\end{matrix} + EtOH = CO_2Et\cdot CHR\cdot C_2H_4\cdot CHR'\cdot CO_2Et.$$

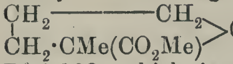
By means of this method, the authors have prepared α-methyl-δ-*iso*propyladipic acid and δ-methyl-α-*iso*propyladipic acid ; the two products, however, were identical, and consisted of a crystalline acid, m. p. 110—111°, and an isomeric liquid, which was probably the eutectic mixture of the two stereoisomerides (compare Crossley and Perkin, Trans., 1898, **73**, 23 ; Martine, Abstr., 1902, i, 629 ; Blanc, Abstr., 1905, i, 681). M. A. W.

Syntheses by means of Methyl and Ethyl Adipates. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1908, **146**, 138—139). —Methyl adipate is transformed by sodamide into the sodium derivative of *methyl* cyclo*pentanonecarboxylate*,



$$\begin{matrix}CH_2 - CH_2\\ CH_2\cdot CH(CO_2Me)\end{matrix}>CO.$$

The latter ester is a colourless liquid with a sweetish odour, b. p. 105°/19 mm., D_4^0 1·145. Its *semicarbazone* forms colourless crystals, m. p. 167°. The sodium compound, when treated with methyl iodide, gives *methyl methyl*cyclo*pentanone*-1-*carboxylate*,

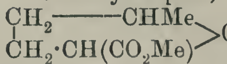


$$\begin{matrix}CH_2 - CH_2\\ CH_2\cdot CMe(CO_2Me)\end{matrix}>CO,$$

a liquid having b. p. 105—106°/15 mm., D_4^0 1·103, which is insoluble in alkalis, and does not form a copper derivative, but forms a *semicarbazone*, brilliant spangles, m. p. 187°. If in the preparation of methyl methyl*cyclo*pentanonecarboxylate the temperature is allowed to rise, *methyl α-methyladipate*,

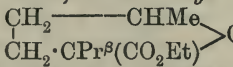
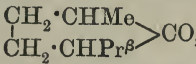
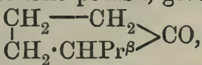
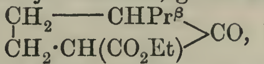
$$CO_2Me\cdot[CH_2]_3.CHMe\cdot CO_2Me,$$

a liquid, b. p. 112—114°/10 mm., D_4^0 1·054, is formed. This is converted by cold aqueous ammonia into *α-methyladipodiamide*, which forms small white crystals, m. p. 186·5°. By the action of sodamide on methyl α-methyladipate, *methyl methyl*cyclo*pentane*-2-*one*-3-*carboxylate*,



$$\begin{matrix}CH_2 - CHMe\\ CH_2\cdot CH(CO_2Me)\end{matrix}>CO,$$

is formed. This is a liquid, b. p. 113—114°/19 mm., which forms a *semicarbazone*, m. p. 118°.

Ethyl methyl*cyclo*pentanone-1-carboxylate (Bouveault, Abstr., 1900, i, 171), when heated with sodium ethoxide, is converted into *ethyl α-methyladipate*, a liquid, b. p. 132—134°/15 mm., D_4^0 1·010, which reacts with sodamide giving *ethyl methyl*cyclo*pentane-2-one-3-carboxylate*, a colourless liquid, b. p. 105°/12 mm., D_4^0 1·057; this gives a non-crystallisable semicarbazone. The sodium compound of the latter ester, on treatment with an *iso*propyl halide, forms *ethyl methyl*-3-iso*propyl*cyclo*pentane-2-one-3-carboxylate*,  $\begin{matrix}CH_2\text{——}CHMe\\ CH_2\cdot CPr^{\beta}(CO_2Et)\end{matrix}>CO$, b. p. 123—124°/10 mm., which, when heated with alcoholic potash, gives *methyl*-3-iso*propyl*cyclo*pentane-2-one*,  $\begin{matrix}CH_2\cdot CHMe\\ CH_2\cdot CHPr^{\beta}\end{matrix}>CO$, a liquid, b. p. 181°, of a camphor-like odour. This forms a *semicarbazone*, m. p. 210°, and an *oxime*, b. p. 127°/22 mm., and is found to be identical with dihydrophorone. But by heating ethyl methyl-3-*iso*propyl*cyclo*pentanonecarboxylate with sodium ethoxide (1 mol.) dissolved in absolute alcohol, at 150° in an autoclave, *ethyl α-methyl-δ*-iso*propyladipate*, $CO_2Et\cdot CHMe\cdot[CH_2]_2\cdot CHPr^{\beta}\cdot CO_2Et$, b. p. 144—146°/14 mm., is formed, and on saponification gives the corresponding *acid*, m. p. 110—111°, b. p. 215—220°/14 mm. *Ethyl* 1-iso*propyl*cyclo*pentanonecarboxylate*, prepared by the method used for the methyl compound, is difficult to obtain pure; it is a liquid, b. p. 141—143°/27 mm., which gives a *semicarbazone*, m. p. 141—142°. The ester, when saponified by alcoholic potash, gives a small quantity of 1-iso*propyl*cyclo*pentane-2-one*,  $\begin{matrix}CH_2\text{—}CH_2\\ CH_2\cdot CHPr^{\beta}\end{matrix}>CO$, a liquid, b. p. 174°, with a pleasant camphor-like odour, which forms a *semicarbazone*, m. p. 200—201°, but the chief product consists of Blanc's *α-iso*propyladipic acid (Abstr., 1905, i, 681), b. p. 222°/12 mm., m. p. 66—67°. The *ethyl* ester, a liquid having b. p. 148—149°/17 mm., D_4^0 0·9876, when condensed by sodamide, gives *ethyl* iso*propyl*cyclo*pentane-2-one-3-carboxylate*,  $\begin{matrix}CH_2\text{——}CHPr^{\beta}\\ CH_2\cdot CH(CO_2Et)\end{matrix}>CO$, b. p. 132—136°/14 mm., D_4^0 1·028. The latter is easily methylated, giving *ethyl* 1-*methyl*-3-iso*propyl*cyclo*pentane-2-one*-1-*carboxylate*, a liquid, b. p. 128—129°/12 mm., D_4^0 1·027, which behaves like its isomeride towards alcoholic potash and sodium ethoxide. α-Methyladipic and α-methyl-δ-*iso*propyladipic acids have been characterised by Locquin's method (Abstr., 1904, i, 644). *Methyl-α-ketol α-methyladipate*,

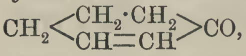
$$COMe\cdot CH_2\cdot CO_2\cdot CHMe\cdot[CH_2]_3\cdot CO_2\cdot CH_2\cdot COMe,$$

b. p. 230°/12 mm., forms a *disemicarbazone*, m. p. 157—160° (decomp.). *Methyl-α-ketol α-methyl-δ*-iso*propyladipate*,

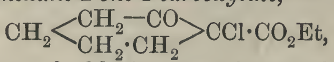
$$COMe\cdot CH_2\cdot CO_2\cdot CHMe\cdot[CH_2]_2\cdot CHPr^{\beta}\cdot CO_2\cdot CH_2\cdot COMe,$$

b. p. 230°/12 mm. (approx.), gives a *disemicarbazone*, m. p. 162° (decomp.). E. H.

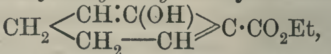
Transitions from Hydroaromatic to Aromatic Compounds. I. Phenol and Salicylic Acid from Hydrobenzene Derivatives. Arthur Kötz and C. Götz (*Annalen*, 1907, 358, 183—204). —A study of the relation of the hydroaromatic to the aromatic derivatives of the six carbon atom ring. The work of previous authors has shown that these hydroaromatic compounds are converted into the corresponding benzene derivatives by intramolecular change, as that of triketohexamethylene into trihydroxybenzene, or by dehydrogenation, when the hydrogen may be removed as a hydrohaloid, as water, or as hydrogen sulphide. The present paper gives an account of the gradual conversion of *cyclo*hexanol (hexahydrophenol) and *cyclo*hexane-2-ol-1-carboxylic acid (hexahydrosalicylic acid) into phenol and salicylic acid respectively. Schemes are given showing the various intermediate substances transformable into each other by intramolecular change and formed in the stages of the gradual dehydrogenation by means of halogens. This transformation of hydroaromatic into aromatic compounds is a reversal of Sabatier and Senderens' reduction of phenol and of the reduction of salicylic acid by means of sodium and alcohol, but differs from these in that it permits of the isolation of the intermediate products.

The action of 1 mol. of bromine or chlorine on 1 mol. of *cyclo*hexanol in presence of water and calcium carbonate leads to the formation of *cyclo*hexanone, whilst if 2 mols. of the halogen are employed, *2-bromo*cyclo*hexane-1-one*, C_6H_9OBr, is formed. This is obtained also in a 60—65% yield by the action of bromine on *cyclo*hexanone, as a strongly refracting oil, b. p. 89—90°/14 mm., and gradually decomposes, evolving hydrogen bromide on exposure to air. When treated with aniline in anhydrous ethereal solution, 2-bromo*cyclo*hexanone loses hydrogen bromide and yields *Δ²-*cyclo*hexenone*,  $CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH=CH\end{matrix}>CO$, which is obtained as a mobile oil, b. p. 63°/14 mm., decolorises permanganate instantaneously, and forms a *semicarbazone*, crystallising in prisms, m. p. 161°. The action of 1 mol. of bromine on the unsaturated ketone in carbon disulphide solution leads to the formation of hydrogen bromide and phenol.

*Ethyl 1-chloro*cyclo*hexane-2-one-1-carboxylate*,



$$CH_2<\begin{matrix}CH_2-CO\\ CH_2\cdot CH_2\end{matrix}>CCl\cdot CO_2Et,$$

formed by the action of chlorine on ethyl *cyclo*hexane-2-one-1-carboxylate (Kötz and Michels, Abstr., 1906, i, 666), cooled by ice, is obtained as an oil, b. p. 138—139°/13 mm., which has a sharp odour and does not give a blue coloration with ferric chloride. The corresponding *bromo*-ester, $C_9H_{13}O_3Br$, is obtained as a light yellow oil, b. p. 144°/13 mm., has a suffocating odour, and on distillation under the ordinary pressure yields *ethyl 2-hydroxy-Δ^{2:6}-*cyclo*hexadienecarboxylate* (*Δ^{2:6}-dihydrosalicylate*),  $CH_2<\begin{matrix}CH:C(OH)\\ CH_2-CH\end{matrix}>C\cdot CO_2Et$, b. p. 104—105°/13 mm., which decolorises potassium permanganate and gives a brown coloration with ferric chloride. The *acid*, $C_7H_8O_3$, crystallises in white leaflets, and sublimes in needles, m. p. 128°.

*Ethyl 1-bromo-2-hydroxy-Δ^{2:5}-*cyclo*hexadienecarboxylate*, $C_9H_{11}O_3Br$, formed by the action of bromine on ethyl dihydrosalicylate in carbon disulphide solution cooled with ice, is obtained as a yellow oil, b. p. 155°, under reduced pressure, and, when distilled under the ordinary pressure, evolves hydrogen bromide and yields ethyl salicylate.

The action of 2 mols. of bromine on ethyl *cyclo*hexane-2-one-1-carboxylate and hydrolysis of the product leads to the formation of 3-*bromosalicylic acid*, $C_7H_5O_3Br$, which sublimes in needles, m. p. 184°. G. Y.

Substances which play a Part in the Synthesis of Salicylic Acid. JACOB MOLL VAN CHARANTE (*Rec. trav. chim.*, 1908, 27, 58—77).—The theory is put forward that in the synthesis of sodium salicylate, sodium phenoxide (2 mols.) and carbon dioxide (1 mol.) first form an additive product of the type $C(OPh)_2(ONa)_2$, which, after a molecular transposition into a salicylic derivative, decomposes into sodium salicylate and sodium phenoxide, or basic sodium salicylate and phenol (compare Claisen, Abstr., 1905, i, 258). This view is supported by the formation of sodium salicylate and phenetole when ethyl phenyl carbonate is heated with sodium phenoxide (Hentschel, Abstr., 1883, 588), and the production of sodium salicylate by heating sodium phenoxide and sodium ethyl carbonate in sealed tubes at 200° (Schmitt, Abstr., 1885, 982). The author confirms the observations of Hentschel, that phenyl carbonate, when heated at 180°—190° with sodium phenoxide (2 mols.) in a current of dry hydrogen, gives neither diphenyl ether nor salicylic acid, and of Schmitt, that sodium phenyl carbonate is converted quantitatively into sodium salicylate when heated in a sealed tube at 120°, but, having repeated Bruyn and Tymstra's experiments, fails to confirm their results (Abstr., 1905, i, 209, 439). According to the theory of these authors, after heating sodium phenyl carbonate at 100°, there should be no excess pressure within the tube, whereas this is invariably observed.

When sodium phenyl carbonate is treated with dry acetone in an apparatus arranged to prevent access of atmospheric moisture (a detailed description is given in the paper), carbon dioxide is evolved, and the residue contains phenol and sodium (as normal and basic carbonate) in the proportions required by the equation $3ONa{\cdot}CO{\cdot}OPh + 2H_2O = 3Ph{\cdot}OH + CO_2 + Na_2CO_3 + NaHCO_3$. All external water having been excluded, that used in the reaction probably arises from condensation of the acetone, but no such condensation product was detected. Sodium phenoxide dissolves in boiling acetone, from which it crystallises on cooling in needles containing $1\frac{1}{2}$ mols. of acetone, which is lost in a vacuum over sulphuric acid. Sodium salicylate dissolves in about 21 parts of acetone at 16°, but the basic salt is insoluble. In acetone, sodium salicylate has the abnormally high molecular weight 282.

When sodium phenyl carbonate is heated in a sealed tube in a boiling water-bath for 100 hours and the product treated with acetone in the above apparatus, carbon dioxide is evolved corresponding with 50—60% of unchanged sodium phenyl carbonate, and the residue contains about 14% of phenol and about 10% of sodium salicylate. No basic sodium salicylate and no additive product were observed, the latter possibly having been decomposed by the acetone. The suggestion is made that the sodium phenoxide *o*-carboxylic acid described by Bruyn and Tymstra is really an additive compound of the nature proposed by the author. E. H.

Preparation of Alkylaminoalkyl Esters of Salicylic Acid. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 188571).—The alkylaminoalkyl salicylates, which combine anæsthetic properties with those of salicylic acid, may be prepared by the following three methods: esterification of salicylic acid with alkylamino-alcohols, interaction of alkylamines and the salicylates of the chlorohydrins, interaction of alkylamino-alcohols and the salicylides.

β-Diethylaminoethyl salicylate, $C_6H_4(OH)\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$, a colourless oil, results from the interaction of diethylaminoethyl alcohol and salicylic acid or salicylide, the former condensation being effected with hydrogen chloride at 115—120°, and the latter with the two reagents alone at 160°; it is also produced by heating salicylic acid and ethyleneglycolchlorohydrin with a small amount of sulphuric acid and then boiling the resulting β-chloroethyl salicylate with diethylamine; its *hydrochloride* separates from acetone as a white, crystalline mass, m. p. 146°.

Piperidylethyl salicylate, obtained by condensing salicylic acid and β-hydroxyethylpiperidine with hydrogen chloride at 115—120°, yields a *hydrochloride*, m. p. 174°, which separates from acetone in white crystals. G. T. M.

The Supposed Phenylhydrazone of Salicylic Acid. Hans Meyer (*Monatsh.*, 1907, **28**, 1381—1384).—It was shown previously (Abstr., 1904, i, 251) that salicylaldehyde neutralises 75% of a molecular proportion of alkali. This influence of an ortho-substituting group on the acidity of a phenol has been studied in other similar cases, and some of the results obtained are now published. As is well known, the phenolic hydroxyl of salicylic acid is almost neutral, salicylic acid neutralising only one equivalent of alkali. This must be ascribed to the influence of the group, $\cdot CO_2M'$, which is positive, not negative as is that of the carboxylic group. Hence the acidity of the phenolic hydroxyl must increase as the $\cdot OM'$ in the group CO_2M' is substituted by a less positive group. In agreement with this view, it is found that whilst methyl salicylate is almost neutral, the following derivatives of salicylic acid neutralise varying amounts of alkali, as indicated by the figures given, which are percentages of an equivalent of base: phenylsalicylate (salol), 30; α-naphthyl salicylate (alphol), almost 40; saligenin, 20; salicylamide, over 90; salicylanilide, about 95.

Schrötter and Flooh's supposed phenylhydrazone of salicylic acid (Abstr., 1907, i, 929) is salicylphenylhydrazide, m. p. 131°, which is best prepared by heating wintergreen oil with phenylhydrazine and phenylhydrazine hydrochloride; it neutralises almost one equivalent of alkali. G. Y.

Formation of Organic Nitro-compounds by the Action of Ammoniacal Silver Oxide Solution. Heinrich Brunner and Rudolf Mellet (*J. pr. Chem.*, 1908, [ii], **77**, 25—33. Compare Brunner, Abstr., 1902, i, 452; 1905, i, 59).—It is now found that the action of ammoniacal silver oxide solution on salicylaldehyde in presence of sodium hydroxide leads to the formation of two nitrosalicylic acids, which are separated by means of their barium salts.

3-*Nitrosalicylic acid*, $C_7H_5O_5N$, crystallises in white needles containing water of crystallisation, m. p. 144° (when anhydrous), and gives a blood-red coloration with ferric chloride. The *barium* salt forms orange-yellow needles.

5-*Nitrosalicylic acid* crystallises in anhydrous needles, m. p. 228°, and gives a red coloration with ferric chloride, and the indophenol reaction with soda-lime. The *barium* salt crystallises in yellow prisms, and is more soluble than its isomeride in water.

Under similar conditions, *m*-methoxysalicylic, *p*-hydroxybenzoic and dibromosalicylic acids, and dibromosalicylaldehyde form nitro-derivatives, but in quantities too small to permit of their isolation. Phenol, benzaldehyde and dextrose, on the other hand, are not nitrated in this manner. The mechanism of the reaction is discussed.

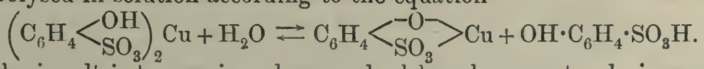
G. Y.

Preparation of Thiosalicylic Acid. LEOPOLD CASSELLA and Co. (D.R.-P. 189200).—Thiosalicylic acid, $SH\cdot C_6H_4\cdot CO_2H$, is obtained in almost quantitative yield by heating *o*-chlorobenzoic acid with strong aqueous sodium hydroxide (1 mol. NaOH) and potassium hydrosulphide at 150—200° in the presence of a small amount of copper sulphate or finely divided copper. As the water evaporates, the temperature of the mixture is raised to 250° until the mass becomes solid. The product is then dissolved in water, and thiosalicylic acid precipitated by mineral acids as a yellowish-white, crystalline precipitate.

This reaction may also be effected in closed vessels by heating the mixture at 200—250° for six to twelve hours. G. T. M.

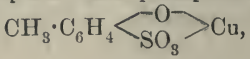
Formation of Salts and Complex Salts with Organic Acids containing the Hydroxyl Group. HEINRICH LEY and O. ERLER (*Zeitsch. anorg. Chem.*, 1908, 56, 401—421).—The authors have investigated by physico-chemical methods the copper salts of the phenolsulphonic, *o*-cresolsulphonic and hydroxybenzoic acids, and the compounds formed by the action of ammonia and pyridine on these salts. Evidence has been obtained that the phenolic hydroxyl group has a tendency to salt-formation, more particularly in the compounds containing ammonia and pyridine.

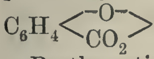
The aqueous solution of *copper* p-*phenolsulphonate* is deep blue in colour, and is highly dissociated into $Cu^{\cdot\cdot}$ and phenolsulphonate ions. Solutions of the corresponding salt of *o-phenolsulphonic acid* are yellowish-green in colour, which seems to indicate a different constitution from the *p*-compound. It was found, however, that the $Cu^{\cdot\cdot}$ ion concentration is much the same in both cases, but the *o*-salt is hydrolysed in solution according to the equation



$$\left(C_6H_4{<}\begin{matrix}OH\\SO_3\end{matrix}\right)_2Cu+H_2O \rightleftharpoons C_6H_4{<}\begin{matrix}-O-\\SO_3\end{matrix}{>}Cu+OH\cdot C_6H_4\cdot SO_3H.$$

The basic salt is brown in colour, and, although present only in small concentration, masks the blue colour of the $Cu^{\cdot\cdot}$ ions. It has been isolated by the action of dilute ammonia on the solution of the copper salt, and crystallises in needles with $2H_2O$.

The copper salts of *o*-cresol-*o*-sulphonic and -*p*-sulphonic acids behave similarly; the basic *o*-cresol salt,  $CH_3\cdot C_6H_4<\begin{matrix}-O-\\SO_3\end{matrix}>Cu$, forms small, yellowish-green leaflets.

Of the copper salts of the hydroxybenzoic acids, only copper salicylate was sufficiently soluble for investigation in aqueous solution. The solution is intensely green in colour, probably owing to some extent to partial hydrolysis with production of the greenish-yellow basic salt,  $C_6H_4<\begin{matrix}-O-\\CO_2\end{matrix}>Cu$, already isolated by Piria (1855).

By the action of ammonia on copper salicylate, two compounds were obtained. One, occurring in green needles, has the formula

$$Cu(O\cdot C_6H_4\cdot CO_2\cdot NH_4)_2,$$

the copper being present as complex anion; the other, obtained with more dilute ammonia, has the formula

$$OH\cdot Cu\cdot O\cdot C_6H_4\cdot CO_2H,2NH_3,2H_2O,$$

but its constitution has not been established with certainty. A pyridine compound of copper salicylate, $(OH\cdot C_6H_4\cdot CO_2)_2Cu,2C_5NH_5$, has been obtained in small, light-blue, columnar needles; its constitution has not been elucidated.

When ammonia is added in considerable excess to a solution of copper *p*-hydroxybenzoate, the solution finally becomes blue, and then contains the copper as complex $Cu(NH_3)_2^{\cdot\cdot}$ and $Cu(NH_3)_4^{\cdot\cdot}$ ions. From the solution, the *compound*, $(OH\cdot C_6H_4\cdot CO_2)_2Cu,2NH_3$, was isolated in dark-blue leaflets.

The behaviour of copper *m*-hydroxybenzoate with ammonia is between that of the ortho- and para-compounds; with very concentrated ammonia, a solution containing complex copper cations is obtained.

The *pyridine* compound of copper *p*-hydroxybenzoate,

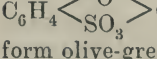
$$(OH\cdot C_6H_4\cdot CO_2)_2Cu,2C_5NH_5,$$

occurs in bluish-violet needles.

Corresponding results were obtained for the action of ammonia and pyridine on the copper phenolsulphonates and *o*-cresolsulphonates. From the solutions of the *p*-sulphonates, treated with ammonia in excess, the salts, $(OH\cdot C_6H_4\cdot SO_3)_2Cu,4NH_3,2H_2O$, and

$$(OH\cdot C_6H_3\cdot CH_3\cdot SO_3)_2Cu,4NH_3,2H_2O,$$

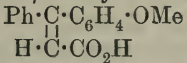
were obtained in bluish-violet needles. Migration experiments showed that the copper in these solutions is present as a complex cation, probably $Cu(NH_3)_4^{\cdot\cdot}$. The *pyridine* salts, $(OH\cdot C_6H_4\cdot SO_3)_2Cu,4C_5NH_5$, and $(OH\cdot C_6H_3\cdot CH_3\cdot SO_3)_2Cu,4C_5NH_5$, also occur in blue needles.

The *o*-sulphonates, with excess of ammonia, only give green solutions, from which the two salts, $OH\cdot Cu\cdot O\cdot C_6H_4SO_3H,2NH_3,2H_2O$, and $OH\cdot Cu\cdot O\cdot C_6H_3Me\cdot SO_3H,2NH_3,2H_2O$, were obtained in dark green needles. Their constitution has not been elucidated, but migration experiments show that at least one ammonia group is present as an $NH_4^{\cdot}$ ion. The corresponding *pyridine* salts,  $C_6H_4<\begin{matrix}-O-\\SO_3\end{matrix}>Cu,2C_5NH_5,H_2O$, and $OH\cdot Cu\cdot O\cdot C_6H_3Me\cdot SO_3H,2C_5NH_5$, form olive-green needles.

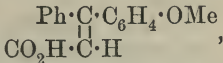
The green anions containing copper are much more stable in the ortho- than in the para-compounds, which is probably due to the fact that the phenolic hydroxyl group is more acidic when the carboxyl or sulphonic group is in the para- than when in the ortho-position. G. S.

Action of Nascent Hypoiodous Acid (Iodine and Sodium Carbonate) on Some Acids of the General Formula $CHR{:}CH{\cdot}CH_2{\cdot}CO_2H$ (R being Phenyl more or less substituted). J. Bougault (*Compt. rend.*, 1908, **146**, 140—142).—It has been shown previously (Abstr., 1905, i, 9; 1906, i, 848) that the unsaturated acids having a single double linking in the $\beta\gamma$ or $\gamma\delta$ position give iodo-lactones when their alkali salts are treated in aqueous solution with iodine. The yield of iodo-lactone is diminished by the presence of sodium carbonate, and a large excess of this salt totally inhibits its formation. Phenyl*iso*crotonic acid, $CHPh{:}CH{\cdot}CH_2{\cdot}CO_2H$, in dilute aqueous solution, with a large excess of sodium carbonate, gives von Pechmann's benzoylacrylic acid, $COPh{\cdot}CH{:}CH{\cdot}CO_2H$ (Abstr., 1882, 1074), when treated with iodine dissolved in potassium iodide solution. Benzoylacrylic acid, on oxidation with alkaline permanganate, gives benzoic and oxalic acids, and, on reduction with sodium amalgam, γ-hydroxyphenylbutyric acid, $OH{\cdot}CHPh{\cdot}[CH_2]_2{\cdot}CO_2H$. It combines with hydrogen bromide and chloride, giving bromo- and chloro-phenylbutyric acids, the first of which is reduced by zinc and acetic acid to benzoylpropionic acid. The action of hypoiodous acid on phenyl*iso*crotonic acid differs from that on anethole (Abstr., 1902, i, 452) in that twice as much oxygen is absorbed in the former as in the latter case. Application of the reaction to *p*-methoxyphenyl*iso*crotonic acid gives a yellow acid, m. p. 131°, which is probably *p*-methoxybenzoylacrylic acid. E. H.

Stereoisomeric β-Arylcinnamic Acids. Richard Stoermer and E. Friderici (*Ber.*, 1908, **41**, 324—343).—*o*-Methoxybenzophenone reacts with ethyl bromoacetate in the presence of zinc yielding ethyl β-phenyl-β-*o*-anisylhydracrylate, $OMe{\cdot}C_6H_4{\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2Et$, which reacts with a mixture of acetyl chloride and acetic anhydride yielding ethyl β-*o*-anisylcinnamate, $OMe{\cdot}C_6H_4{\cdot}CPh{:}CH{\cdot}CO_2Et$; the ester thus obtained appears to be homogeneous, and has the configuration corresponding with formula II. When hydrolysed with alcoholic potash and precipitated with dilute mineral acid, a mixture of the two stereoisomeric β-anisylcinnamic acids,

I. α-acid 

$$\begin{array}{c} Ph{\cdot}C{\cdot}C_6H_4{\cdot}OMe \\ \| \\ H{\cdot}C{\cdot}CO_2H \end{array}$$

II. β-acid 

$$\begin{array}{c} Ph{\cdot}C{\cdot}C_6H_4{\cdot}OMe \\ \| \\ CO_2H{\cdot}C{\cdot}H \end{array},$$

is obtained. These may be separated by fractional crystallisation from benzene. The two acids are stereoisomeric, as their esters have the same b. p.; both acids yield *β-phenyl-β-anisylpropionic acid*, m. p. 131°, when reduced, and the β-acid is readily transformed into the α-acid when exposed to sunlight or ultra-violet light. The acids do not combine with bromine, and when solutions of their sodium salts are treated with bromine water, carbon dioxide is evolved, and α-phenyl-*o*-anisylbromoethylene (m. p. 78·5°, Stoermer and Simon, Abstr., 1905, i, 53) is obtained. The silver salts, when treated with iodine, yield *phenylanisyliodoethylene*, m. p. 84°, which appears to exist in one modification only. The configurations of the two acids have been deduced from the relatively positive and negative nature of the substituents, from their relative strengths, and also from the action of acetyl chloride on the two acids. The acetyl chloride hydrolyses the methoxy-group; the α-acid is hydrolysed more readily, and yields the anhydride, phenylcoumarin. The β-acid is also hydrolysed, but less readily; it is shown that the hydrolysis is preceded by molecular rearrangement, and the final product is also phenylcoumarin. *Ethyl β-phenyl-β-o-anisylhydracrylate* has b. p. 190—196°/7 mm., and solidifies to a crystalline mass, m. p. 57·5—58°. When distilled under higher pressures, it shows a tendency to lose water, and then does not solidify readily. The corresponding *acid* has m. p. 139°, and when melted evolves carbon dioxide and water. The *barium* salt dissolves in alcohol, and has m. p. 225°. *Ethyl β-o-anisylcinnamate* has b. p. 215—220°/20 mm., and dissolves in concentrated sulphuric acid to an intense olive-green solution.

β-o-*Anisylcinnamic acid* (α-acid) crystallises from benzene in slender, colourless needles containing a molecule of benzene. It melts at 146°, but if previously heated at 80—95° to remove the benzene it melts at 153°. The stereoisomeric acid also crystallises with benzene, but when heated previously at 80—95° melts at 118°.

The solubilities in alcohol are α, 1·33; β, 3·75; in benzene, α, 0·67; β, 3·3, and in carbon disulphide, α, 0·51; β, 2·4; the numbers indicating % of dissolved material.

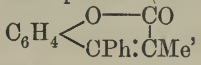
The sodium salt of the α-acid is readily soluble in alcohol or water, is hygroscopic, and has m. p. 255°; the isomeric β-salt can be crystallised from water, in which it is somewhat sparingly soluble, and has m. p. 105° in the hydrated, or 282° in the anhydrous, state. Both salts, when decomposed with acetic, carbonic, or hydrochloric acids, yield the α-acid; the β-acid can, however, be obtained from the β-sodium salt if it is finely divided and mixed with *N*/10 solution of hydrogen chloride or oxalic acid in ether. The *β-silver* salt is crystalline, and has m. p. 170° (decomp.); the α-salt amorphous, and is solid at 300°. Both are unaffected by light. The *α-pyridine* salt, obtained by boiling the acid with water and pyridine, has m. p. 62°, and readily loses pyridine. The *β-pyridine* salt, m. p. 83°, is more stable. Aniline yields a salt with the β-acid only. The *α-piperidine* salt has m. p. 54—55°; the *β-piperidine* salt is less soluble, has m. p. 194°, and is very stable.

When esterified by saturating their alcoholic solutions with hydrogen chloride, both acids yield the same ester, and this, on hydrolysis, yields mainly the β-acid, the small amount of α-acid being due to the transforming action of the mineral acid used in precipitating the acids. The α- and β-esters are best prepared by the action of methyl sulphate on the sodium salts. The *α-methyl* ester crystallises from methyl alcohol in compact prisms, m. p. 58°, and, on hydrolysis, yields the α-acid. The *β-methyl* ester has been obtained as an oil only, and when hydrolysed gives a mixture of both acids. In the presence of aqueous ammonia, the β-ester is transformed into the α-compound.

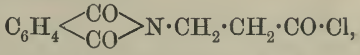
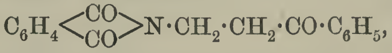
β-Phenylcoumarin, $C_{15}H_{10}O_2$, crystallises from alcohol in slender, colourless needles, m. p. 105°. It does not give a coloration with ferric chloride, and dissolves in sodium hydroxide solution, the addition of acids precipitating the unaltered coumarin. The solution of the sodium salt reacts with methyl sulphate, yielding the methyl ester of the methoxy-acid, m. p. 58°.

α-Methoxybenzophenone, ethyl α-bromopropionate, and zinc yield *ethyl β-anisyl-α-methyl-β-phenylhydracrylate*,

$$OMe{\cdot}C_6H_4{\cdot}CPh(OH){\cdot}CHMe{\cdot}CO_2Et,$$

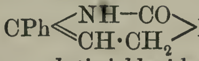
m. p. 65°, and from this two stereoisomeric *β-o-anisyl-α-methylcinnamic acids*, $OMe{\cdot}C_6H_4{\cdot}CPh{:}CMe{\cdot}CO_2H$, m. p. 139° and 110°, have been prepared. The chief product of hydrolysis is, however, *β-phenyl-α-methylcoumarin*,  $C_6H_4<\begin{matrix}O\text{—}CO\\ CPh{:}CMe\end{matrix}$, m. p. 79°. *Ethyl β-o-hydroxyphenyl-α-methylhydracrylate*, $OH{\cdot}C_6H_4{\cdot}CPh(OH){\cdot}CHMe{\cdot}CO_2Et$, obtained from *o*-hydroxybenzophenone, zinc, and ethyl α-bromopropionate, crystallises from alcohol, and has m. p. 136°. J. J. S.

Derivatives of the Amino-acids Applicable for Synthetical Purposes. SIEGMUND GABRIEL (*Ber.*, 1908, 41, 242—250. Compare Abstr., 1907, i, 625).—Phthalylglycyl chloride and α-bromo-β-phthalyl alanine are very reactive, and can be used for synthetical purposes. Phthalylglycyl chloride (*loc. cit.*) can be distilled in vacuum without change, but decomposes at atmospheric pressure, forming carbon monoxide and chloromethylphthalimide.

β-Phthalylalanyl chloride,  $C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>N{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}Cl$, obtained from phthalylalanine and phosphorus pentachloride, forms a bright yellow oil, solidifying to a crystalline mass, m. p. 107—108°. It reacts with benzene in presence of aluminium chloride to form *β-phthaliminopropiophenone*,  $C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>N{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$, crystallising in faint yellow, rhombic plates, m. p. 130—131°. When heated at 150° under pressure with acetic and hydrochloric acids, this forms *β-aminopropiophenone hydrochloride*,

$$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5,NH_2,$$

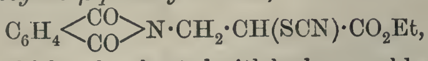
which crystallises in large, flat prisms, m. p. 128°, does not reduce Fehling's solution, and forms a *picrate*, long needles, m. p. 155°, and a *platinichloride*, separating in concentrically-arranged yellow needles, which sinter at 200°, m. p. 215° (decomp.).

β-Aminopropiophenone reacts with potassium cyanate to form *propiophenonylcarbamide*, $COPh{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$, consisting of long needles, m. p. 129°. When heated with sulphuric acid, it is probably converted into an anhydro-compound, *oxyphenyldihydropyrimidine*,  $CPh<\begin{matrix}NH\text{—}CO\\ CH{\cdot}CH_2\end{matrix}>NH$, forming three- and four-sided plates, and giving a *platinichloride*, which darkens about 260°. *Propiophenonylphenylthiocarbamide*, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NHPh$, forms flat, six-sided plates, m. p. 90°.

α-Bromo-β-phthalylalanine is converted by heating with hydrogen bromide into *α-bromo-β-alanine hydrobromide*,

$$NH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H,HBr.$$

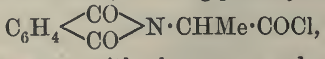
Of the phthalyl compound, the *methyl* ester has m. p. 52—53°; the *ethyl* ester, 48—50°. These, on heating with potassium thiocyanate, form *ethyl α-thiocyano-β-phthalylalanine*,



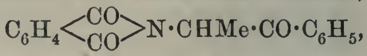
$$C_6H_4<\substack{CO\\CO}>N\cdot CH_2\cdot CH(SCN)\cdot CO_2Et,$$

m. p. 83—85°, which, when heated with hydrogen chloride, is converted into *iso*cysteine.

α-Phthalylalanine reacts with bromine and phosphorus to form tribromoethylphthalimide (compare Sachs, Abstr., 1898, i, 476), and with phosphorus pentachloride, forming *phthalylalanyl chloride*,



$$C_6H_4<\substack{CO\\CO}>N\cdot CHMe\cdot COCl,$$

m. p. 73°. This reacts with benzene and aluminium chloride, forming α-phthaliminopropiophenone,  $C_6H_4<\substack{CO\\CO}>N\cdot CHMe\cdot CO\cdot C_6H_5$, separating in colourless, stellar, aggregates of needles and prisms, m. p. 87—88° (compare Schmidt, Abstr., 1890, 372), and yields α-aminopropiophenone, previously described by Behr-Bregowski (Abstr., 1897, i, 459). The picrate is now found to have m. p. 164—165°; the platinichloride, m. p. 205—206°.

Phenacylphthalimide has m. p. 167°, and not 155° as previously given. E. F. A.

Phenylmalononitrile. II. JOHN C. HESSLER (*Amer. Chem. J.*, 1908, **39**, 63—80).—In the first paper on this subject (Abstr., 1904, i, 830), an account was given of the preparation of phenylmalononitrile, and it was stated that the silver salt rapidly decomposes with formation of a white, amorphous substance, m. p. 147—148°. It has now been found that at least three compounds are formed by the decomposition of this salt, namely, bisphenylmalononitrile, trisphenylmalononitrile, and a substance, m.p. about 210—230°.

Bisphenylmalononitrile, probably $CN\cdot CPh(CH{:}NH)\cdot CPh(CN)_2$, m. p. 87—88°, forms nearly colourless crystals, and separates from benzene in large, white plates, $(C_9H_6N_2)_2,C_6H_6$, m. p. 67—68°. The *silver* salt, $C_{18}H_{11}N_4Ag$, is stable at the ordinary temperature, but decomposes at 90°. The *ethyl* derivative, $CN\cdot CPh(CH{:}NEt)\cdot CPh(CN)_2$, m. p. 101—102°, crystallises in plates. The n-*butyl* derivative has m. p. 80—81°.

The compound (m. p. 147—148°) described previously is probably trisphenylmalononitrile, $(C_9H_6N_2)_3$.

The third compound formed by the decomposition of the silver salt is an amorphous *substance*, $(C_9H_5N_2)x$, m. p. 210—230° (decomp.), which can also be obtained by the oxidation of phenylmalononitrile or either of its polymerides with chromic acid. It also formed together with small quantities of another *substance*, m. p. 117—118°, by the action of bromine on the sodium derivative of the nitrile.

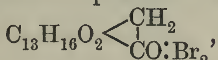
Phenylmethylmalononitrile, $CPhMe(CN)_2$, b. p. 125—130°/16 mm., is obtained as an oil by the action of methyl iodide on the sodium derivative.

When the sodium derivative of phenylmalononitrile is treated with a solution of diazobenzene chloride, an unstable product is obtained, which is decomposed by ether with evolution of nitrogen and formation of a white *substance*, m. p. 107°.

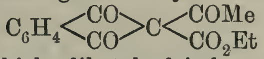
a-Cyanophenylacetanilide, m. p. 136°, crystallises in needles. The o-, m-, and p-*toluidides* melt at 139°, 131°, and 139° respectively. The *phenylhydrazide* has m. p. 224°.

When an alcoholic solution of phenylmalononitrile is treated with hydrochloric acid, cyanophenylacetic acid, amide, and ethyl ester are produced, together with ammonium chloride.

Attempts were made to prepare ethyl cyanophenylacetate by the elimination of carbon monoxide from ethyl cyanophenylpyruvate (Erlenmeyer, Abstr., 1893, i, 37), but without success. E. G.

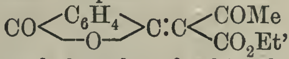
Santonin. X. Bromination of Santonin. EDGAR WEDEKIND [with MARTIN RÖDIGER] (*Ber.*, 1908, **41**, 359—366. Compare Abstr., 1907, i, 137).—The bromination of santonin has been again studied, and the cause of the differences in the observations of Klein (Abstr., 1893, i, 112; 1907, i, 421) and of Wedekind and Koch (Abstr., 1905, i, 212) determined. Klein's colourless product, obtained on bromination of santonin in acetic acid in presence of 5—10% of water, is santoninoxonium dibromide,  $C_{13}H_{16}O_2<\begin{matrix}CH_2\\ CO{:}Br_2\end{matrix}$, and if freshly prepared yields santonin on treatment with an alkali. When mixed with santonin and hydrogen bromide in molecular proportions in glacial acetic acid or chloroform solution, it forms a red solution resembling that of Wedekind and Koch's hydroperbromide, which is formed on bromination of santonin in glacial acetic acid solution. The formation of bromosantonin by the action of aniline on santonin dibromide is confirmed. When exposed to light for three days in aqueous bromine solution, santonin forms a product, decomposing about 100°, which is a mixture of santonin and santonin dibromide. G. Y.

Structure of Phthalacene. GIORGIO ERRERA (*Gazzetta*, 1907, **37**, ii, 624—636).—Ethyl phthalaconecarboxylate, $C_{21}H_{11}O_2\cdot CO_2Et$, prepared by the action of sodium acetate on a mixture of phthalic anhydride and ethyl acetoacetate, is accompanied by tribenzoylenebenzene (compare Michael, Abstr., 1906, i, 518). According to the author, this reaction gives firstly an intermediate compound of the form:

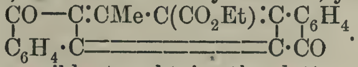


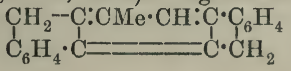
$$C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>C<\begin{matrix}COMe\\ CO_2Et\end{matrix}$$

or

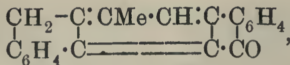


$$CO<\begin{matrix}C_6H_4\\ O\end{matrix}>C{:}C<\begin{matrix}COMe\\ CO_2Et\end{matrix},$$

from which diketohydrindene is formed, 2 mols. of this then condensing to anhydrobisdiketohydrindene. One mol. of the latter may then condense with either a third mol. of diketohydrindene, giving tribenzoylenebenzene, or a mol. of ethyl acetate, yielding ethyl phthalaconecarboxylate,  $\begin{array}{l}CO-C{:}CMe\cdot C(CO_2Et){:}C\cdot C_6H_4\\ C_6H_4\cdot C=\!=\!=\!=\!=\!=\!=\!=\!=C\cdot CO\end{array}$. It has, however, not been found possible to obtain the latter from either ethyl phthalylacetoacetate, ethyl sodiohydrindenecarboxylate, diketohydrindene, or anhydrobisdiketohydrindene. Phthalacene (compare Gabriel, Abstr., 1884, 1176, 1189) is regarded as

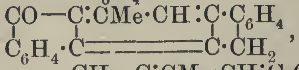


$$\begin{array}{l}CH_2-C{:}CMe\cdot CH{:}C\cdot C_6H_4\\ C_6H_4\cdot C=\!=\!=\!=\!=\!=C\cdot CH_2\end{array};$$

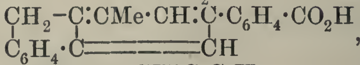
the oxide of phthalacene as 

$$\begin{array}{l} CH_2-C{:}CMe\cdot CH{:}C\cdot C_6H_4 \\ C_6H_4\cdot C=\!=\!=\!=\!=C\cdot CO \end{array}$$

, or

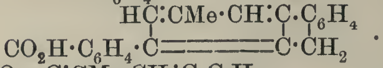


$$\begin{array}{l} CO-C{:}CMe\cdot CH{:}C\cdot C_6H_4 \\ C_6H_4\cdot C=\!=\!=\!=\!=C\cdot CH_2 \end{array}$$

, and phthalacenic acid as 

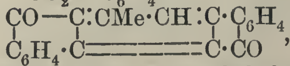
$$\begin{array}{l} CH_2-C{:}CMe\cdot CH{:}C\cdot C_6H_4\cdot CO_2H \\ C_6H_4\cdot C=\!=\!=\!=\!=CH \end{array}$$

, or



$$\begin{array}{l} HC{:}CMe\cdot CH{:}C\cdot C_6H_4 \\ CO_2H\cdot C_6H_4\cdot C=\!=\!=\!=\!=C\cdot CH_2 \end{array}$$

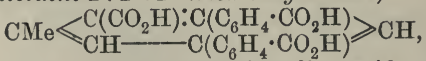
.

Phthalacone, 

$$\begin{array}{l} CO-C{:}CMe\cdot CH{:}C\cdot C_6H_4 \\ C_6H_4\cdot C=\!=\!=\!=\!=C\cdot CO \end{array}$$

, prepared by the action of excess of potassium dichromate on phthalacene in acetic acid solution or by dry distillation of phthalaconecarboxylic acid either alone or mixed with zinc dust, crystallises from acetic acid in minute, yellow needles, m. p. 257—259°, and dissolves sparingly in the ordinary solvents.

3 : 5-*Diphenyltoluene*-2 : 2′ : 2″-*tricarboxylic acid,*

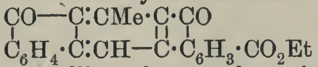


$$CMe{<}\begin{array}{l} C(CO_2H){:}C(C_6H_4\cdot CO_2H) \\ CH\text{———}C(C_6H_4\cdot CO_2H) \end{array}{>}CH,$$

prepared by fusing phthalaconecarboxylic acid with potassium hydroxide, exists in two modifications, one amorphous and readily soluble in alcohol, acetic acid, or ethyl acetate, whilst the other crystallises from acetic acid in granules, m. p. 212—215°, and is sparingly soluble in the above solvents. The *calcium* salt,

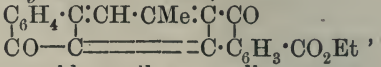
$$(C_{22}H_{13}O_6)_2Ca_3,$$

also exists in an amorphous and a crystalline $(+14H_2O)$ condition. The *diethyl* ester, $CO_2H\cdot C_6H_2Me(C_6H_4\cdot CO_2Et)_2$, m. p. 189—190°; *triethyl* ester, $C_{28}H_{28}O_6$, m. p. 152—153°; *trimethyl* ester, $C_{25}H_{22}O_6$, m. p. 198°, and the *monoethyl* ester, $CO_2Et\cdot C_6H_2Me(C_6H_4\cdot CO_2H)_2$, m. p. 258°, were prepared. The action of concentrated sulphuric acid on this acid yields another acid, the *ethyl* ester of which,



$$\begin{array}{l} CO-C{:}CMe\cdot C\cdot CO \\ C_6H_4\cdot C{:}CH-C\cdot C_6H_3\cdot CO_2Et \end{array}$$

or



$$\begin{array}{l} C_6H_4\cdot C{:}CH\cdot CMe{:}C\cdot CO \\ CO-C=\!=\!=\!=\!=C\cdot C_6H_3\cdot CO_2Et \end{array}$$

, crystallises from xylene in minute, golden-yellow needles, m. p. 295—297°.

T. H. P.

Onocerin (Onocol). II. Franz von Hemmelmayr (*Monatsh.*, 1907, **28**, 1385—1399. Compare Abstr., 1906, i, 356).—When titrated with potassium hydroxide in alcoholic solution with phenolphthalein as indicator, onoceric acid requires for neutralisation about 20 per cent. more alkali than calculated for a monobasic acid of the formula $C_{20}H_{30}O_4$, whilst the methoxyl determination with the *methyl* ester, m. p. 68—80°, prepared by the action of methyl alcohol and hydrogen chloride or concentrated sulphuric acid on onoceric acid, gives results about 2 per cent. less than that required for the formula $C_{21}H_{32}O_4$. When heated with acetic anhydride and sodium acetate, onoceric acid yields a white, amorphous *product*, $C_{40}H_{58}O_7$, which gradually melts when heated, and forms onoceric acid when boiled with dilute alkalis. The action of bromine on onoceric acid in cold glacial acetic acid solution leads to the formation of a white, amorphous *product*,

m. p. 125—130°, containing an amount of bromine lying between $C_{28}H_{30}O_4Br_2$ and $C_{20}H_{29}O_4Br_3$. A *product*, $C_{20}H_{28}O_4Br_4$, is formed by the action of bromine on onoceric acid in boiling glacial acetic acid solution.

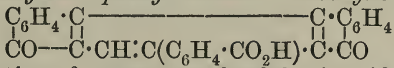
When oxidised by means of potassium permanganate in cold glacial acetic acid solution, onocerin yields *dihydroxyonoketone*, $C_{26}H_{40}O_4$, which is obtained as a white, amorphous mass, m. p. 65—70°, and forms a *diacetate*, $C_{30}H_{44}O_6$, and a *diphenylhydrazone*, $C_{38}H_{52}O_2N_4$, m. p. 120° (decomp.). On oxidation with potassium permanganate in boiling glacial acetic acid solution, onocerin yields an amorphous *acid*, $C_{26}H_{38}O_6$, which melts gradually above 90°, and forms an amorphous *silver* salt, $C_{26}H_{37}O_6Ag$.

On treatment with bromine in cold glacial acetic acid solution, onocerin yields a mixture of *products*, m. p. 100—130°, which contain amounts of bromine varying between those required for the formulæ $C_{26}H_{44}O_2Br_4$ and $C_{26}H_{43}O_2Br_5$. G. Y.

Structure of Phenenyltribenzoic [1 : 3 : 5-Triphenylbenzene-2′:2″:2‴-tricarboxylic] Acid. GIORGIO ERRERA (*Gazzetta*, 1907, **37**, ii, 618—623).—The author finds that phenenyltribenzoic acid (compare Gabriel and Michael, Abstr., 1878, 734) is readily esterified by Fischer's method, an observation which supports the structure suggested by the above authors. If it were triphenyltrimesic acid, $C_6Me_3(CO_2H)_3$ (Lanser, Abstr., 1899, i, 916), it would not be esterified by alcohol in presence of sulphuric acid. The author also confirms Michael's refutation (Abstr., 1906, i, 518) of Manthey's statement (Abstr., 1901, i, 31) that the acid is 2 : 4-diphenyl*cyclo*butadiene-1 : 3-dicarboxylic acid.

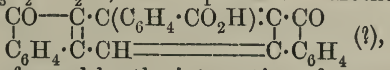
Triethyl phenenyltribenzoate, $C_6H_3(C_6H_4\cdot CO_2Et)_3$, was obtained only as an uncrystallisable gum.

3 : 4 : 5 : 6-*Dibenzoylene*-1-*phenylbenzene*-2′-*carboxylic acid*,



$$\begin{array}{l} C_6H_4\cdot C\text{————————}C\cdot C_6H_4 \\ \vert \qquad\ \Vert \qquad\qquad\qquad\qquad\qquad\quad \Vert \quad \vert \\ CO\text{—}C\cdot CH{:}C(C_6H_4\cdot CO_2H)\cdot C\cdot CO \end{array}$$

, obtained by the action of concentrated sulphuric acid on phenenyltribenzoic acid, crystallises from alcohol in golden-yellow, silky needles containing 1Et·OH ; m. p. of alcohol-free substance, 349—350° ; the *ethyl* ester, $C_{26}H_{13}O_2\cdot CO_2Et$, has m. p. 253°. Another *acid*,



$$\begin{array}{l} CO\text{—}C\cdot C(C_6H_4\cdot CO_2H){:}C\cdot CO \\ \vert \qquad \Vert \qquad\qquad\qquad\qquad\quad \vert \quad \vert \\ C_6H_4\cdot C\cdot CH\text{=======}C\cdot C_6H_4 \end{array}$$

(?), m. p. 321°, is also formed by the interaction of concentrated sulphuric acid and phenenyltribenzoic acid. T. H. P.

[Condensation Products of Tannic Acid and Formaldehyde with the Phenols.] HERMANN HILDEBRANDT (D.R.-P. 188318).—Condensation products of tannic acid, formaldehyde, and the phenols result when an alcoholic solution of the phenol, mixed with an aqueous solution of tannic acid, is treated successively with excess of formaldehyde and concentrated hydrochloric acid.

Tanninphenolmethane, a flocculent, white powder, insoluble in alcohol but dissolving in alkaline solutions, does not melt below 240°

Tanninthymolmethane and *bromotanninthymolmethane* are slightly coloured powders, soluble in alcohol, and decomposing respectively at 235° and 200°. Similar products are obtained from bromotannic acid and formaldehyde with phenol, *o*-cresol, and *β*-naphthol. G. T. M.

Methyl Tannin. JOSEF HERZIG (*Ber.*, 1908, **41**, 33).—Dekker's contention (Abstr., 1906, i, 686) that the author's analytical data for methyl tannin agree better for a hexamethyl derivative, is due to an arithmetical error. A methoxyl determination, moreover, shows it to be pentamethyl tannin. W. R.

Coffee. I. K. GORTER (*Annalen*, 1908, **358**, 327—348).—The account given of the author's study of the constituents of coffee extract is prefaced by a résumé of the work of previous investigators. On evaporation, the alcoholic extract of Liberian coffee yields crystalline potassium-caffeine chlorogenate, $C_{32}H_{36}O_{19}K_2,(C_8H_{10}O_2N_4)_2,2H_2O$ (Payen, *Annalen*, 1846, **60**, 286), in amounts equivalent to 3·3% of the coffee. This substance crystallises in almost white prisms, becomes yellow at 150°, and brown at 225°, but does not melt, yields an alkaline ash on incineration, and loses caffeine when shaken with moist chloroform. *Chlorogenic acid*, $C_{32}H_{38}O_{19}$, is obtained by action of lead acetate on the aqueous solution of the double compound and treatment of the precipitated basic lead salt with hydrogen sulphide, or by addition of sulphuric acid to convert the potassium into the sulphate and extraction of the caffeine with chloroform. The acid crystallises in needles, m. p. 206—207°, $[\alpha]_D - 33{\cdot}1°$, can be titrated with alkalis as a dibasic acid, reduces silver nitrate when heated, but has only a slight action on Fehling's solution, gives colour reactions with the alkalis and alkaline earths, ferric chloride, uranyl acetate, and zinc chloride, and does not react with semicarbazide or phenylhydrazine. The *calcium*,

$$C_{32}H_{36}O_{19}Ca,6\tfrac{1}{2}H_2O,$$

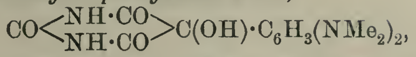
magnesium, ($5H_2O$), *zinc*, ($5H_2O$), *lead*, ($2H_2O$), *basic lead*,

$$C_{32}H_{36}O_{19}Pb,2PbO,$$

benzidine, *basic benzidine*, $C_{32}H_{38}O_{19}(C_{12}H_{12}N_2)_2,10H_2O$, and *strychnine*, $(C_{32}H_{38}O_{19})_2(C_{21}H_{22}O_2N_2)_3,2H_2O$, salts are described. G. Y.

Tetramethyl-2 : 4-diaminobenzaldehyde. FRANZ SACHS and ERNST APPENZELLER (*Ber.*, 1908, **41**, 91—108).—The only polyaminobenzaldehyde hitherto known, obtained by Sachs and Kempf (Abstr., 1902, i, 682) by the reduction of 2 : 4-dinitrobenzaldehyde, showed neither the properties of an aldehyde nor of a *m*-diamine, owing to internal condensation to an aldehyde ammonia compound. To prevent such condensation, a diaminobenzaldehyde has been prepared, in which all the amine hydrogens were replaced. Starting from *m*-phenylenetetramethyldiamine, attempts were made to obtain an aldehyde by heating it with formaldehyde and *p*-nitrosodimethylaniline (Ullmann and Frey), or with formaldehyde and an aromatic hydroxylamine or its sulphonic acid (Geigy), but without success. Formaldehyde does not even condense with the base in presence of hydrogen chloride to a diphenylmethane derivative.

Alloxanyltetramethyl-m-*phenylenediamine*,



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right\rangle\mathrm{C(OH)\cdot C_6H_3(NMe_2)_2},$$

prepared by Pellizari's method, forms colourless, glistening crystals, which darken at 180°, soften at 205°, and decompose at 223°. When decomposed with hot sulphuric acid, a small quantity of tetramethyldiaminobenzaldehyde is formed. This is more conveniently obtained by condensing the diamine with chloralanhydride to *tetramethyldiaminophenylhydroxytrichloroethane*, $C_6H_3(NMe_2)_2\cdot CH(OH)\cdot CCl_3$, which, without being isolated, is hydrolysed by alkali.

Tetramethyl-2 : 4-*diaminobenzaldehyde* is a yellow, oily liquid of a resin-like odour and biting, bitter taste, b. p. 203°/14 mm., and solidifies to a yellow, hard, crystalline mass, m. p. 8°.

The *mercurichloride* crystallises in pale greenish-yellow tablets ; the *sodium hydrogen sulphite* compound is a grey powder, m. p. 105°. It does not react with hydroxylamine or phenylhydrazine, nor is it attacked by concentrated alcoholic ammonia. The *picrate* sinters at 145°, m. p. 161—162° ; the *semicarbazone*, a yellowish-white mass of needles, has m. p. 215°. *Tetramethyldiaminobenzylidenehydrazine*,

$$C_6H_3(NMe_2)_2\cdot CH{:}N\cdot NH_2,$$

separates from alcohol in glistening, yellow crystals, m. p. 212°.

Ethyl tetramethyl-m-*diaminobenzylidenecyanoacetate*,

$$C_6H_3(NMe_2)_2\cdot CH{:}C(CN)\cdot CO_2Et,$$

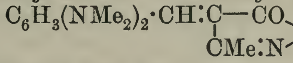
prepared by condensation of the acid with ethyl cyanoacetate, forms yellow, glistening crystals, m. p. 110—112°. *Tetramethyl*-2 : 4-*diaminobenzylideneacetophenone*, $C_6H_3(NMe_2)_2\cdot CH{:}CH\cdot COPh$, is a reddish-yellow oil, of which the *picrate* crystallises in orange needles, which sinter at 158°, m. p. 163°.

Tetramethyldiaminobenzylidenemalonitrile, $C_6H_3(NMe_2)_2\cdot CH{:}C(CN)_2$, crystallises in orange-yellow needles, m. p. 166°.

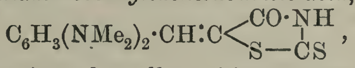
Tetramethyl-2 : 4-*diaminobenzylidene*-p-*nitrobenzyl cyanide*,

$$C_6H_3(NMe_2)_2\cdot CH{:}C(CN)\cdot C_6H_4\cdot NO_2,$$

forms glistening, red needles, m. p. 170°.

4 - *Tetramethyl*-2′ : 4′-*diaminobenzylidene* - 1 - *phenyl* - 3 - *methyl* - 5-*pyrazolone*,  $\mathrm{C_6H_3(NMe_2)_2\cdot CH{:}}\begin{array}{l}\mathrm{C{-}CO}\\ \mathrm{CMe{:}N}\end{array}\!\!\!>\mathrm{NPh}$, prepared by condensation of the aldehyde with phenylmethylpyrazolone, forms minute, matted, reddish-yellow needles, m. p. 181°.

Tetramethyl-2 : 4-*diaminobenzylidenerhodanic acid*,



$$\mathrm{C_6H_3(NMe_2)_2\cdot CH{:}C}\left\langle\begin{array}{l}\mathrm{CO\cdot NH}\\ \mathrm{S{-}CS}\end{array}\right.,$$

separates in microscopic, red needles, which sinter at 198°, and slowly melt at 208°.

On mixing the dilute hydrochloric acid solution of the components and warming, the aldehyde gives with phloroglucinol a very characteristic, red *hydrochloride*, $C_6H_3(NMe_2)_2\cdot CH[C_6H_2(OH)_3]_2,2HCl$, which has no melting point, and is insoluble in all solvents but pyridine or acetic acid, but dissolves in alkali hydroxides to a red solution with green fluorescence. The free *base* is a brown, indistinctly crystalline substance, which becomes lighter in colour when dried, and analysis indicates partial elimination of water, forming $C_{23}H_{24}O_5N_2$.

The aldehyde reacts with a diazotised solution of *m*-nitroaniline, forming m-*nitrobenzeneazotetramethyl*-2 : 4-*diaminobenzaldehyde*,

$$NO_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_2(NMe_2)_2\cdot CHO,$$

a brownish-yellow powder, m. p. 158°.

By reaction with magnesium ethyl bromide, *tetramethyldiaminophenylethylcarbinol* is formed as an oil, which on distillation yields *propenyltetramethyl*-m-*phenylenediamine*, a yellow oil which crystallises when cooled, but melts at the room temperature. The *picrate* forms intensely yellow, microscopic crystals, which sinter at 138°, m. p. 142°.

Tetramethyl-2 : 4-*diaminotriphenylmethane* forms pale brown tablets, m. p. 122—123°. E. F. A.

p-Tolylacetaldehyde and its Derivatives. K. Kling (*Bull. Acad. Sci. Cracow*, 1907, 448—453. Compare Auwers and Keil, Abstr., 1903, i, 100, 620).—p-*Tolylacetaldehyde*, $C_6H_4Me\cdot CH_2\cdot CHO$, is obtained on distilling barium *p*-tolylacetate with barium formate under 17—50 mm. pressure. It forms a white, crystalline substance, m. p. about 40°, b. p. 221—222°/760 mm. (partial decomp.) or 109°/17 mm., has a characteristic odour, gives Tollens' aldehyde reaction, is oxidised slowly on exposure to air, forming *p*-tolylacetic acid, and forms an *additive* compound with sodium hydrogen sulphite. The *aldoxime*, $C_9H_{11}ON$, crystallises in colourless prisms, m. p. 126—126·5°. The *thiosemicarbazone*, $C_9H_{10}{:}N\cdot NH\cdot CS\cdot NH_2$, crystallises in colourless, rhombic scales, and forms a *silver* salt, $C_{10}H_{12}N_3SAg$, which was analysed. Reduction of the aldehyde or the acid in alcoholic sulphuric acid solution, with a lead cathode and an electric current of 2·6 amperes per sq. dm. density, at 20—40° leads to the formation of primary *p*-tolylethyl alcohol, $C_6H_4Me\cdot CH_2\cdot CH_2\cdot OH$, b. p. 244—245°. Ciesielski's product, b. p. 220—221° (Abstr., 1907, i, 409), was probably a mixture of the primary and secondary alcohols. G. Y.

A Method of Preparation of Cyclic Aldehydes. Savariau (*Compt. rend.*, 1908, **146**, 297—298).—Blaise and Bagard (Abstr., 1904, i, 369) have shown that acyclic acid-alcohols are decomposed by heat, giving aldehydes. The author has applied this method to the preparation of cyclic aldehydes. Aryl organo-magnesium compounds condense with chloral, giving trichloro-secondary aryl alcohols, which are transformed by alkalis into acid-alcohols, or, in some cases, into the aldehydes themselves. Jocitsch's $\beta\beta\beta$-trichloro-α-phenylethyl alcohol, $CCl_3\cdot CHPh\cdot OH$, when boiled with a saturated solution of potassium carbonate, gives benzaldehyde, chloroform, and phenylglycollic acid (65%). The latter when heated gives 47% of benzaldehyde, and leaves a residue containing diphenylmaleic anhydride, formed by condensation, and phenylacetic acid, probably resulting from the reduction of phenylglycollic acid by the formic acid produced in its decomposition.

Chloral condenses with the magnesium derivative of bromo-*p*-xylene, giving $\beta\beta\beta$-*trichloro*-α-*xylylethyl alcohol*, $CCl_3\cdot CH(C_6H_3Me_2)\cdot OH$, a light yellow, viscous liquid, b. p. 158°/10 mm., which on prolonged boiling with potassium carbonate solution gives xylylaldehyde, $C_6H_3Me_2\cdot CHO$ (compare Bouveault, Abstr., 1899, i, 286; Harding and Cohen, Abstr., 1901, i, 725). The following derivatives of this aldehyde are described: *semicarbazone*, fine, white needles, m. p. 217°; p-*nitrophenylhydrazone*, small, red crystals, m. p. 182°; *phenylbenzylhydrazone*, small, light yellow needles, m. p. 103°; p-*xylylidene-β-naphthylamine*, nacreous lamellæ, m. p. 86—87°, and p-*xylylidenecyanoacetic acid*, m. p. 174°. E. H.

Friedel and Crafts' Reaction. VIII. Successive Substitution of the Atoms of Chlorine in Carbon Tetrachloride by Aromatic Groups. Jacob Böeseken (*Rec. trav. chim.*, 1908, 27, 5—9).—The fact that the chief product of the action of benzene on carbon tetrachloride in the presence of aluminium chloride is dichlorodiphenylmethane and that no trace of trichlorophenylmethane can be detected (Abstr., 1905, i, 423, 583) can be explained either by the simultaneous substitution of the first two atoms of chlorine, or by the rapidity of the second of the two reactions: $CCl_4 + C_6H_6 = CPhCl_3 + HCl$; $CPhCl_3 + C_6H_6 + CPh_2Cl_2 + HCl$.

By reacting with carbon tetrachloride in the presence of aluminium chloride and subsequent heating of the product with a mixture of sulphuric and glacial acetic acids, *o*-dichlorobenzene gives 3 : 4-dichlorobenzoic acid and 3 : 4 : 3′ : 4′-*tetrachlorobenzophenone*, m. p. 142°; *m*-dichlorobenzene gives 2 : 4-dichlorobenzoic acid and 2 : 4 : 2′ : 4′-*tetrachlorobenzophenone*, m. p. 78°; *p*-dichlorobenzene gives 2 : 5-dichlorobenzoic acid and Norris and Green's 2 : 5 : 2′ : 5′-tetrachlorobenzophenone (Abstr., 1902, i, 379); whilst *p*-dibromobenzene gives 2 : 5-dibromobenzoic acid. The yields of the acids are small. The conclusion is drawn that the second explanation is correct, and this is in accordance with many other reactions of carbon tetrachloride (compare Besson, Abstr., 1894, i, 481; Goldschmidt, Abstr., 1881, 707; Radziszewski, Abstr., 1884, 1133; Klason, Abstr., 1887, 1015). E. H.

Friedel and Crafts' Reaction. IX. Condensation of the Dihalogen Derivatives of Benzene with Acetyl and Benzoyl Chlorides under the Influence of Aluminium Chloride. Jacob Böeseken (*Rec. trav. chim.*, 1908, 27, 10—15).—When a mixture of a benzene derivative with an acyl chloride is acted on by aluminium chloride, two distinct reactions may take place: (1) Friedel and Crafts' reaction; (2) Combe's condensation (Abstr., 1887, 127), thus:

$$3CH_3\cdot COCl + AlCl_3 = CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot COCl,AlCl_3 + 2HCl.$$

These two reactions generally have very different velocities; in the case of the benzene derivatives, in which the substituting group increases the activity of the remaining hydrogen atoms of the benzene nucleus, the second reaction is so slow as to be practically non-existent, but, when the substituting group diminishes the activity of the hydrogen atoms, the velocity of Friedel and Crafts' reaction my become equal to, or less than, that of the second condensation. The condensation of polyhalide derivatives of benzene with acetyl chloride is an instance of the latter kind, the second reaction having the greater velocity, in consequence of which only very small quantities of the ketones are formed. *o*-Dichlorobenzene gives 2% of *o*-dichloroacetophenone, whilst *m*-dichlorobenzene gives only 0·4% of the corresponding ketone, and other polyhalogenbenzenes give no trace of ketone (identifiable by oxidation). On the other hand, benzoyl chloride, which does not react with aluminium chloride below 170°, condenses with *o*- and *m*-dichloro- and dibromo-benzenes, giving 80—90% yields of the dichloro- and dibromo-benzophenones. *p*-Dichloro- or dibromo-benzene is not attacked below 200°, at which temperature a black, tarry product results. E. H.

Hydrolysis of Phenolic Ethers. RICHARD STOERMER and, in part, E. FRIDERICI and H. ALTGELT (*Ber.*, 1908, **41**, 321—324. Compare Auwers, Abstr., 1907, i, 919, 1033).—*o*-Hydroxybenzophenone cannot be obtained by boiling the methyl ether with concentrated hydrochloric acid (Edelstein and Kostanecki, Abstr., 1905, i, 460), and even at 120° only a small amount is formed. The hydroxy-ketone may be obtained quite readily by dissolving the methoxy-compound in four times its weight of glacial acetic acid, adding concentrated hydrobromic acid (48%) so long as the ketone is not precipitated, and then boiling the mixture for 1·5 hours. The product is diluted, neutralised with sodium carbonate, and extracted with ether. *p*-Methoxybenzophenone, *o*-*p*-dianisyl ketone, anisole, *p*-bromoanisole, *o*-bromoanisole, anisic acid, and phenyl-*p*-anisylpropylene are readily hydrolysed; *p*-methoxybenzophenone yields 28·6% of the hydroxy-compound after two hours. Vanillin yields 38% of protocatechualdehyde, and *m*-methoxybenzophenone only a small amount of hydroxybenzophenone, whereas *o*-methoxybenzaldehyde and dianisylethylene yield resins. J. J. S.

2:5-Dihydroxybenzophenone. JOSEF HERZIG and BR. HOFMANN (*Ber.*, 1908, **41**, 143—145).—2:5-Dimethoxybenzophenone is pure white, as recorded by Hantzsch and Blackler (Abstr., 1906, i, 857), and not yellow as stated by Kauffmann and Grombach (Abstr., 1906, i, 283); the latter authors' statement that this compound cannot be converted by hydriodic acid into 2:5-dihydroxybenzophenone is incorrect. The monomethyl ether obtained by the partial hydrolysis of 2:5-dimethoxybenzophenone and described by Kauffmann and Grombach (*loc. cit.*) as 5-hydroxy-2-methoxybenzophenone may also be prepared by the action of diazomethane on 2:5-dihydroxybenzophenone. Since it is formed in this manner and is, moreover, yellow and but sparingly soluble in alkalis, the authors consider it probable that this compound is really 2-*hydroxy*-5-*methoxybenzophenone* (compare Herzig, Abstr., 1891, 1349; Graebe and Eichengrün, Abstr., 1892, 1224).

W. H. G.

Preparation and Purification of Tetrachlorobenzoquinone (Chloroanil) and Tetrachloroquinol (Hydrochloroanil). LOUIS BOUVEAULT (*Ann. Chim. Phys.*, 1908, [viii], **13**, 142—144. Compare Abstr., 1899, i, 790).—When commercial chloroanil (Schuchardt) dissolved in fuming nitric acid is treated with potassium chlorate, the lower chloro-derivatives of quinone, which constitute the chief impurity, are converted into higher chloro-derivatives, and a mixture of tri- and tetra-chlorobenzoquinones containing traces of the mono- and di-chloro-derivatives is obtained. After removing the latter by distillation in steam, the mixture is dissolved in acetic acid and saturated with dry hydrogen chloride; this converts the trichlorobenzoquinone into tetrachloroquinol, and the resulting mixture of tetrachloroquinol and tetrachlorobenzoquinone can be converted into the quinol derivative by reduction with stannous chloride, or into the quinone derivative by oxidation with nitric acid, the final product in each case weighing more than the original crude substance. M. A. W.

Tribromomethoxy-*o*-benzoquinone Methylhemiacetal. C. Loring Jackson and H. A. Flint (*Amer. Chem. J.*, 1908, **39**, 80—87).—It was shown by Jackson and MacLaurin (Abstr., 1907, i, 856) that tetrachloro- and tetrabromo-*o*-quinones behave differently towards methyl alcohol, and this was attributed to the chlorine of the former substance being attacked whilst the bromine of the latter was not. It is now found, however, that, although the halogen of the tetrabromo-compound is much less liable to attack than that of the tetrachloro-compound, it is affected to a very small extent. This has been proved by the observation that when the tetrabromo-compound is treated with cold methyl alcohol, a small quantity of *tribromomethoxy-*o*-benzoquinone methylhemiacetal*, $OH\cdot C_6Br_3O(OMe)_2$, m. p. 138°, is produced and crystallises in yellow plates. This substance is obtained as the main product when tetrabromo-*o*-benzoquinone is boiled with methyl alcohol for one and a-half to two hours. The *acetyl* derivative, m. p. 158°, forms pale yellow crystals, and yields a *phenylhydrazone*, m. p. 205°, which crystallises in nearly white needles. When the hemiacetal is heated with hydrobromic acid, it is converted into *tribromohydroxy-*p*-benzoquinone*, $C_6Br_3O_2\cdot OH$, m. p. 205°, which forms red plates. If hydrochloric acid is used instead of hydrobromic acid, a mixture of trichloro- and tribromo-hydroxy-*p*-quinones is produced. E. G.

[Direct Production of Alizarin from Anthraquinone.] Badische Anilin- und Soda-Fabrik (D.R.-P. 116526).—In the technical production of alizarin from anthraquinone, the sulphonation sometimes proceeds to the extent of forming a certain proportion of disulphonic acid which either entails a separation of the sulphonic acids or leads to the contamination of the final product with trihydroxyanthraquinones.

It has now been found that anthraquinone may be converted readily into alizarin by one operation, the product being free from by-products and furnishing a remarkably blue shade of alizarin-red. One hundred parts of anthraquinone are mixed with a solution of 300 parts of sodium or potassium hydroxide and 20 to 30 parts of sodium chlorate in 100 parts of water, and heated to 200° either in an open vessel or in an autoclave until the oxidising agent is expended. The mass must be stirred until the operation is complete. The product is dissolved in water, and the hydroxyanthranol present re-converted into anthraquinone by a current of air. The alizarin is then precipitated by milk of lime, the calcium salt decomposed with hydrochloric acid, and the alizarin freed from anthraquinone by dissolving in dilute aqueous sodium hydroxide.

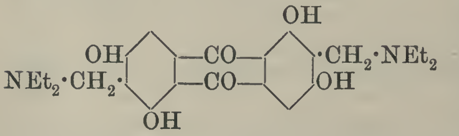
In this operation, sodium chlorate may be replaced by other oxidising agents, such as the peroxides of sodium, barium, manganese, or lead.

G. T. M.

Preparation of Dichloroanthraflavic Acid. R. Wedekind & Co. (D.R.-P. 187685).—Anthraflavic acid cannot be chlorinated in dilute acid solution, but when suspended in a mixture of 160 parts of 50% sulphuric acid heated at 120°, it is readily converted into a new *dichloroanthraflavic acid* (m. p. 362—364°), which yields a *diacetate*, m. p. 292°, and *dibenzoate*, m. p. 318—320°. Although these constants agree with the data obtained for the dichloroanthraflavic acid and its derivatives produced by the action of alkaline hypochlorite on anthraflavic acid, yet the solubilities of the two series of substances are quite different (compare Abstr., 1904, i, 813).

G. T. M.

[Preparation of Amino-derivatives of Anthrachrysone.] Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 188189).—Anthrachrysone (110 parts) dissolved in 180 parts of 30% diethylamine and 1500 parts of water, and treated with 60 parts of 40% formaldehyde at the ordinary temperature, rapidly undergoes transformation into the *diamine* (annexed formula), which separates as a mass of orange-red crystals with a blue reflex. The diethylamine may be replaced by ammonia, methylamine, ethylamine, dimethylamine, or benzylamine. The diamines thus produced are all of the above type, and have the same general properties; they are orange-red, crystalline powders, scarcely soluble in water or the volatile organic solvents, but dissolving in aqueous alkali hydroxides or acids, or in concentrated sulphuric acid, to yellow solutions. They crystallise in well defined forms from chlorobenzene, but have no definite melting point.



G. T. M.

[Thio-derivatives of Anthraquinone.] Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 188605).—4 : 8-Dithiol-1 : 5-dihydroxyanthraquinone, when heated with aromatic amines, such as aniline or *p*-toluidine in the presence of boric acid, gives rise to a green, crystalline condensation product, which contains the original sulphur entirely in the sulphide condition, and has the empirical formula $OH{\cdot}C_6H_3S{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_3S{\cdot}OH$. This substance on sulphonation with fuming acid (10% SO_3) gives rise to a soluble colouring matter, which furnishes very fast shades of green on unmordanted wool.

G. T. M.

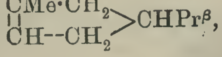
Preparation of Hydroxybenzanthrones. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 187495. Compare Abstr., 1906, i, 889; 1907, i, 324).—Further examination of the benzanthrone condensation has shown that the mono- and poly-anthraquinones and their hydrogenated derivatives, such as β-hydroxyanthranol and leucoquinizarin, condense with glycerol to furnish hydroxybenzanthrones. The condensation is conveniently effected in sulphuric acid, and proceeds most readily with the hydrogenated derivatives of the hydroxyanthraquinones; when, however, the latter are employed, it is preferable to introduce reducing agents, such as ferrous sulphate, zinc, tin, or aniline sulphate.

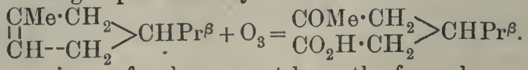
1-*Hydroxybenzanthrone*, yellow needles, m. p. 179·5°, was obtained by heating together, at 150°, 1-hydroxyanthraquinone, glycerol, aniline sulphate, and concentrated sulphuric acid. 2-*Hydroxybenzanthrone*, small yellow crystals, m. p. 291°, was prepared from 2-hydroxyanthranol, glycerol, and concentrated sulphuric acid at 150°, or with zinc chloride as the condensing agent at 180°. G. T. M.

[Chlorination of Dianthraquinonyl Derivatives.] BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 186596. Compare Abstr., 1907, i, 226).—The condensation product of 2:2′-dimethyl-1:1′-dianthraquinonyl can be chlorinated either with free chlorine or sulphonyl chloride when nitrobenzene is employed as a diluent at the ordinary temperature. G. T. M.

Establishment of the Constitutional Formula of Fenchone. LOUIS BOUVEAULT and LEVALLOIS (*Compt. rend.*, 1908, **146**, 180—183).—Since fenchone is a saturated ketone derived from the hydrocarbon $C_{10}H_{18}$, which is therefore dicyclic, whilst Semmler's dihydrofencholenamide (Abstr., 1906, i, 681) is the amide of the acid $C_9H_{17}\cdot CO_2H$ derived from the saturated hydrocarbon C_9H_{18}, necessarily monocyclic, the fixation of ammonia in the action of sodamide on fenchone has resulted in the rupture of one of the two chains in the ketone. When dihydrofencholenamide is treated with bromine and alkali, instead of the expected amine, $C_9H_{17}\cdot NH_2$, for which the name amino*apo*fenchane is proposed, *diapofenchylcarbamide*, $CO(NH\cdot C_9H_{17})_2$, crystals, m. p. 168—169°, is formed. This, when heated with boiling 50% sulphuric acid, decomposes, thus: $CO(NH\cdot C_9H_{17})_2 + H_2SO_4 = CO_2 + (NH_4)_2SO_4 + 2C_9H_{16}$, giving the hydrocarbon apo*fenchene*, C_9H_{16}, H_2O, a liquid, b. p. 143°, D_4^0 0·812, α_D 62°, with a terpenic odour, which forms a *hydrochloride*, b. p. 60°/8 mm., D_4^{18} 0·9275. The separation of ammonia in this decomposition suggests that the NH_2 is attached to a tertiary carbon atom. When oxidised with neutral potassium permanganate solution, *apo*fenchene gives a ketonic *acid*, $C_9H_{16}O_3$, which forms a *semicarbazone*, m. p. 175—177°. The ketonic acid contains the acetyl group, and when treated with alkali and bromine is transformed into bromoform and β-*iso*propylglutaric acid. Since the latter is symmetrical, the ketonic acid must have the constitution

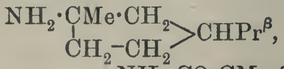
$$COMe\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H,$$

whence the formula of *apo*fenchene is deduced as  $\left.\begin{array}{l}CMe\cdot CH_2\\ \parallel\\ CH{-}{-}CH_2\end{array}\right>CHPr^{\beta}$, its oxidation being represented by

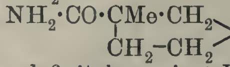
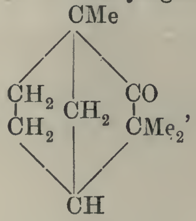


$$\begin{array}{l}CMe\cdot CH_2\\ \|\\ CH{-}{-}CH_2\end{array}\!\!>CHPr^{\beta}+O_3=\begin{array}{l}COMe\cdot CH_2\\ CO_2H\cdot CH_2\end{array}\!\!>CHPr^{\beta}.$$

Accordingly, amino*apo*fenchane must have the formula

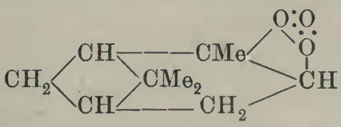


$$\begin{array}{l}NH_2\cdot CMe\cdot CH_2\\ \qquad\; |\\ \qquad CH_2{-}CH_2\end{array}\!\!>CHPr^{\beta},$$

and dihydrofencholenamide that,  $\begin{array}{l}NH_2\cdot CO\cdot CMe\cdot CH_2\\ \qquad\qquad\; |\\ \qquad\qquad CH_2{-}CH_2\end{array}\!\!>CHPr^{\beta}$, proposed by Semmler. This work decides definitely against Wallach's and in favour of Semmler's formula,  , for fenchone.

E. H.

Action of Ozone on Pinene. CARL D. HARRIES and HEINRICH NERESHEIMER (*Ber.*, 1908, 41, 38—42. Compare Abstr., 1906, i, 833).—A solution of pinene in carbon tetrachloride yields, on treatment with ozone, a mixture of two ozonides. About 10% of the hydrocarbon is converted into *pinene perozonide*, forming small, elastic lumps insoluble in all ordinary solvents; it approximately corresponds in composition with the formula $C_{10}H_{16}O_4$, decomposes at 80—85°, and, when decomposed with water, yields liquid pinonic acid (Tiemann and Kerschbaum, Abstr., 1900, i, 625), the semicarbazone of which has m. p. 204°. It changes into a thick, colourless oil when kept a few days in a desiccator; this oil is a mixture of the solid ozonide with a liquid ozonide. The latter compound, *pinene ozonide*, $C_{10}H_{16}O_3$, is the chief product of the action of ozone on pinene; it is a colourless oil, $[\alpha]_D^{20}$ + 11°40′ (52·45% solution in chloroform), D_4^{20} 1·310, and is soluble in most solvents. When boiled with water or 10% aqueous potassium hydroxide or distilled under 12 mm. pressure, it yields an aldehydic substance, probably pinonaldehyde and liquid pinonic acid, b. p. 178—180°, D_4^{15} 1·108, $[\alpha]_D^{22}$ + 12°56′, the semicarbazone of which gave m. p. 203—204° (compare Tiemann and Semmler, Abstr., 1896, i, 308). Since the ozonide yields pinonic acid, it probably has the annexed formula.



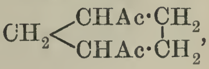
W. H. G.

Constitution of Essential Oils. Derivatives and Constitution of Santene. FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1908, 41, 125—130. Compare Abstr., 1907, i, 703, 1062; 1908, i, 38).—Teresantalic acid is tricyclic, but the constitution of the bicyclic santene has not been fixed, the position of the double linking being still undetermined.

The *benzylidene* derivative of π-norcamphor (Abstr., 1907, i, 1062), $C_{16}H_{18}O$, has b. p. 182—184°/10 mm., D^{20} 1·041, n_D 1·57516; on oxidation with permanganate in acetone solution, *π-norcamphoric acid*, $C_9H_{14}O_4$, is obtained, m. p. 170—171°. The *dimethyl* ester has b. p. 120—123°/9 mm., D^{20} 1·078, n_D 1·46459; the *anhydride* separates in plates, m. p. 107°. *π-Norcamphor oxime* has b. p. 116—120°/9 mm., D^{20} 1·012, n_D 1·49856; it is reduced by sodium in ethyl alcohol to *π-norbornylamine*, $C_9H_{17}N$, b. p. 69°/10 mm., D^{20} 0·9163, n_D 1·47642, which becomes solid when cooled, but melts again at the temperature of the hand. The *picrate* has m. p. 208°; the *oxalate* decomposes at 280°, and the *hydrochloride* has m. p. 272° (decomp.). *π-Norcampholenic acid nitrile*, $C_9H_{13}N$, prepared by heating norcamphoroxime with sulphuric acid, has b. p. 82—83°/9 mm., D^{20} 0·95, n_D 1·472; the *acid*, $C_9H_{14}O_2$, has b. p. 132—134°/10 mm., D^{20} 1·014, n_D 1·47936.

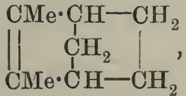
Norborneol with phosphorus pentachloride yields a *chloride*, b. p. 72—73°/10 mm., D^{20} 1·010, n_D 1·48422, m. p. 59—61°. Alcoholic potassium hydroxide eliminates hydrogen chloride from this with ease, forming norcamphene, b. p. 33—35°/10 mm., D^{18} 0·8677, n_D 1·46658, which is identical with santene, as proved by the oxidation to the diketone, $C_9H_{14}O_2$, b. p. 119—124°/10 mm., D^{18} 1·031, n_D 1·47250, whereby an *acid*, m. p. 149—151°, is also formed. When heated with formic acid, santene gives the π-norborneol formate already described (*loc. cit.*), but differing from this in being optically inactive. This formate, on hydrolysis, yields π-norborneol. There is a close analogy between the interconversion of camphene and *iso*borneol, and of santene and π-norborneol. The santenol described by Aschan (this vol., i, 94) is regarded as identical with π-norborneol. E. F. A.

Constituents of Essential Oils. Elucidation of the Constitution of Santene, C_9H_{14}. FRIEDERICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1908, **41**, 385—389).—The results obtained on progressive oxidation of santene confirm the constitution previously suggested for this hydrocarbon (this vol., i, 37, 92). When treated with bromine in sodium hydroxide solution, the diketone, formed on oxidation of santene with ozone or potassium permanganate (*loc. cit.*), yields *cyclo*pentane*trans*dicarboxylic acid, m. p. 86° (Pospischill, Abstr., 1898, i, 636). The *methyl* ester of the *cis*-acid has b. p. 118—120°/9 mm., n_D 1·4576, D^{20} 1·137. It follows that the diketone must be represented by the formula



$$CH_2\Big<\begin{matrix}CHAc\cdot CH_2\\ |\\ CHAc\cdot CH_2\end{matrix},$$

and is derived from santene,



$$\begin{matrix}CMe\cdot CH-CH_2\\ \|\qquad CH_2\qquad |\\ CMe\cdot CH-CH_2\end{matrix}$$

, by resolution of the ethylene linking. Structural formulæ are given showing the relation of santene to teresantalic acid, π-norborneol, π-norborneol chloride, and the diketone with its oxidation product. G. Y.

Thujene and Carvestrene Dihydrohaloids. IWAN L. KONDAKOFF (*J. pr. Chem.*, 1908, [ii], **77**, 135—140. Compare Abstr., 1904, i, 438, 755, 756; 1907, i, 329).—The nature of the dihydrohaloids obtained from thujene is discussed in the light of the results obtained by Wallach (Abstr., 1907, i, 64, 227, 228, 229, 1058, 1061) and by Semmler (Abstr., 1907, i, 145, 329, 714). These substances, previously conceived as dipentene dihydrohaloids, are now considered to be derivatives of terpinene. The liquid dihydrochloride and dihydrobromide are the *cis*-, and the solid isomerides the *trans*-, modifications. Terpinene, prepared from the *trans*-dihydrochloride, has b. p. 174—178°, D^{20} 0·8444, n_D 1·4798, and is optically inactive (compare Abstr., 1904, i, 438). Tschugaeff's and Wallach's terpinenes, obtained by treating the dihydrohaloids with quinoline and aniline respectively, are probably partially isomerised (Abstr., 1900, i, 104). The dihydrobromide prepared from carvestrene is found to be identical with that obtained from thujene. G. Y.

Essential Oil of Brassica rapa var. rapifera. MAX KUNTZE (*Arch. Pharm.*, 1907, **245**, 660—661).—Treatment with alcoholic ammonia yielded phenylethylenethiocarbamide, already observed in other *Cruciferae* and in *Reseda.* G. B.

Essential Oil of Cardamine amara. MAX KUNTZE (*Arch. Pharm.*, 1907, **245**, 657—659).—A slightly impure thiocarbamide, obtained from this oil by treatment with alcoholic ammonia, was identified as *d*-butylthiocarbamide, already described by Urban (Abstr., 1904, i, 376). G. B.

Essential Oil of Magnolia kobus. EUGÈNE CHARABOT and G. LALOUE (*Compt. rend.*, 1908, **146**, 183—185).—From a specimen of the essential oil of *Magnolia kobus* having $\alpha - 1°20'$ (100 mm.), D^{15} 0·9432, the authors have isolated citral (about 15%) and anethole, which is the chief constituent. They suspect the presence of a small quantity of estragole. E. H.

A False Euphorbium Resin. ALEXANDER TSCHIRCH and CARL LEUCHTENBERGER (*Arch. Pharm.*, 1907, **245**, 690—700).—A commercial specimen described as "Gummi Euphorbium" yielded *ψ-euphorbone*, $C_{15}H_{24}O$, colourless crystals, m. p. 116°, $[\alpha]_D$ +48·18°. This substance is closely related to euphorbone from *Euphorbia*, and is either an aldehyde or a ketone. It unites with two atoms of iodine. When fused with potassium hydroxide, it yields phloroglucinol; oxidation with nitric acid gave picric acid, and with alkaline potassium permanganate, a *substance*, $C_{18}H_{28}O$, m. p. 100°. Treatment with sodium and alcohol furnishes a crystalline *substance*, $C_{14}H_{22}O$, m. p. 60°.

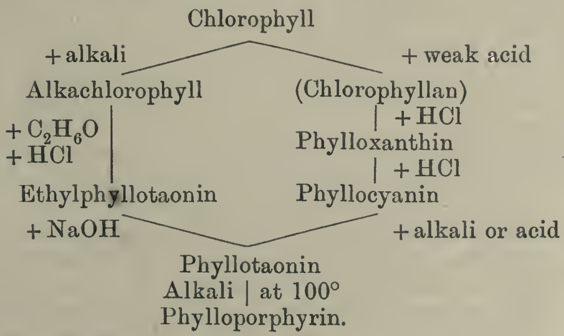
The following amorphous substances were also obtained from the resin: *ψ-Euphorbic acid*, $C_{24}H_{26}O_6$, m. p. 108—109°; *α-ψ-euphorbonic acid*, $C_{14}H_{22}O_{10}$, m. p. 112—113°; *β-ψ-euphorbonic acid*, $C_{18}H_{28}O_{12}$, m. p. 81°, and *ψ-euphorboresen*, $C_{25}H_{64}O_{10}$, m. p. 54—55°. Acid calcium maleate was also present. G. B.

Resin of Pinus Jeffreyi. ALEXANDER TSCHIRCH and CARL LEUCHTENBERGER (*Arch. Pharm.*, 1908, **245**, 701—707).—The following amorphous monobasic acids were obtained from the resin of the Californian Nut Pine (Digger Pine): *a-jeffropinic acid*, $C_{10}H_{14}O_2$, m. p. 160—161°; *β-jeffropinic acid*, $C_{12}H_{18}O_2$, m. p. 80—82°; *a-jeffropinolic acid*, $C_{14}H_{20}O_2$, m. p. 117—118°, and *β-jeffropinolic acid*, $C_{14}H_{20}O_2$, m. p. 77—78°. The first two acids were obtained by extracting the ethereal solution of the resin with ammonium carbonate, the second two with sodium carbonate. G. B.

Amygdalin. Leopold Rosenthaler (*Arch. Pharm.*, 1908, **245**, 684—685).—Since emulsin does not hydrolyse maltose, and since no maltose is formed when emulsin acts on amygdalin, the latter substance cannot be a maltoside, but must be derived from an unknown disaccharide, as suggested by Auld (Proc., 1907, **23**, 72). G. B.

Verbenalin, a New Glucoside from Verbena officinalis. L. Bourdier (*J. Pharm. Chim.*, 1908, [vi], **27**, 49—57, 101—112).—The alcoholic extract of the flowering tops of the common Vervein, when extracted with ethyl acetate, yielded the glucoside *verbenalin*, $C_{17}H_{25}O_{10}$, which separates from ethyl acetate in needles, m. p. 181·5° (corr.), $[\alpha]_D - 180{\cdot}52°$. It is not racemised by baryta at 18°, reduces Fehling's solution, forms crystalline compounds with phenylhydrazine and hydroxylamine, is non-toxic, and is slowly hydrolysed by 2—5% sulphuric acid at 100° and by emulsin to dextrose and an optically inactive, amorphous substance, which is soluble in ether and in sodium hydroxide, reduces Fehling's solution, and gives a violet coloration with ferric chloride. *Verbena officinalis* contains emulsin and invertase. G. B.

The Absorption Spectra of Chlorophyll and its Derivatives. Wilhelm Müllermeister (*Chem. Zentr.*, 1907, ii, 1522; from *Zeitsch. wiss. Photochemie*, 1907, **5**, 339—348).—The spectra of crude chlorophyll, pure chlorophyll, phylloxanthin, phyllocyanin, alkachlorophyll, phyllotaonin, and ethylphyllotaonin have been photographed and measured. The manner in which these chlorophyll derivatives are related to chlorophyll is shown in the annexed scheme:



The results obtained are very different to those described by previous authors (compare Schunck and Marchlewski, Abstr., 1896, i, 574; Koźniewski and Marchlewski, Abstr., 1907, i, 866). G Y.

Chlorophyll. V. Rhodophyllin. Richard Willstätter and Adolf Pfannenstiel (*Annalen*, 1907, 358, 205—265. Compare Abstr., 1907, i, 69, 71, 784, 865).—When heated with alcoholic potassium hydroxide on the water-bath, chlorophyllin salts become strongly fluorescent, at about 140° are transformed into crystalline substances which form blue solutions with intense, red fluorescence, and at about 200° yield deep red products. These derivatives of chlorophyll are magnesium compounds. The reaction product of each stage is a mixture of closely related, similarly coloured substances, which can be separated by the differences in their acid and basic properties.

The red products are termed *rhodophyllins*, and the blue intermediate substances, *glaucophyllins*; of the former, one, which is usually the chief product of the action and is distinguished by its tendency to crystallise and by its solubilities, has been studied specially.

To prepare the rhodophyllin, the chlorophyllin salt is heated with alcoholic potassium hydroxide in an autoclave at 140° and then at 200°, and the *potassium rhodophyllin* precipitated by addition of water. If the chlorophyllin and alkali are heated in a glass tube, the chlorophyll derivatives absorb mineral constituents of the glass; in an experiment in a zinc-glass tube, the magnesium of the chlorophyll was substituted by zinc.

Rhodophyllin, $C_{33}H_{34}O_4N_4Mg$ (?), purified by extraction of the ethereal solution with dilute ammonia, crystallises in glistening, monoclinic prisms containing ether of crystallisation, is stable in air, but becomes hygroscopic after being heated at 105°, forms bluish-red solutions with blood-red fluorescence, and is readily decomposed by acids. The same rhodophyllin is obtained from a number of cryptogamic and phanerogamic plants. In its empirical formula, rhodophyllin approaches Zaleski's formula for hæmin, $C_{34}H_{32}O_4N_4FeCl$ or $C_{34}H_{34}O_4N_4FeCl$ (Abstr., 1903, i, 217), or $C_{33}H_{32}O_4N_4FeCl$, which agrees with the results of Nencki and Zaleski (Abstr., 1901, i, 434) and Küster and Haas (Abstr., 1905, i, 647). The potassium and *magnesium* salts are described.

Alloporphyrin, $C_{33}H_{36}O_4N_4$, the product of the action of acids on rhodophyllin, separates from ether in microscopic needles or leaflets, and dissolves only slowly in concentrated hydrochloric acid when crystalline, but is extracted from its ethereal solution by 8% hydrochloric acid. The *potassium* and *sodium* salts and the *hydrochloride* are described. When heated in acetic anhydride, alloporphyrin forms an *anhydride*, $C_{33}H_{34}O_3N_4$, which crystallises in needles or rhombic leaflets, m. p. above 300° (decomp.), yields a *potassium* salt crystallising in blue prisms, and is extracted from its ethereal solution by 6—7% or, after conversion into the potassium salt and liberation, by 4% hydrochloric acid. Alloporphyrin belongs to the porphyrin group, and has the same composition as mesoporphyrin (Nencki and Zaleski, *loc. cit.*), but is not identical with that substance, as it is insoluble in very dilute hydrochloric acid, but dissolves in the concentrated acid, forms a sodium salt insoluble in aqueous sodium hydroxide, can be regained from its alkaline solutions by acidification and extraction with ether, crystallises on neutralisation of its alkaline or acid solutions in presence of ether, and gives an absorption spectrum differing from that of hæmatoporphyrin both in the intensity and in the position of the bands. G. Y.

Chlorophyll. VI. Crystalline Chlorophyll. RICHARD WILLSTÄTTER and MAX BENZ (*Annalen*, 1908, **358**, 267—287. Compare preceding abstract).—The work of Borodin (*Bot. Zeit.*, 1882, 608) and Monteverde (*Acta Horti Petropolitani*, 1893, **13**, 123) on crystalline chlorophyll has been repeated and confirmed. Details are given of an improved method by which 2·4 grams of crystalline chlorophyll are obtained from 1 kilo. of dried leaves. The colour of the solutions, the spectrum, and the indifference towards dilute acids and alkalis show the crystalline substance to be unchanged chlorophyll; the results obtained on analysis agree best with the formula $C_{38}H_{42}O_7N_4Mg$, and differentiate Borodin's product from the supposed chlorophylls of Hoppe-Seyler (Abstr., 1880, 53), Gautier (Abstr., 1880, 267), Rogalski (Abstr., 1880, 561), and Étard (*La Biochimie et les Chlorophylles*, Paris, 1906), which in their composition approach phaeophytin.

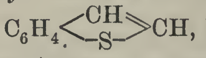
On treatment with oxalic acid, chlorophyll yields magnesium oxalate and *phaeophorbin*, which crystallises, forms olive-brown solutions, yields complex metallic derivatives, and differs from phylloxanthin in forming a zinc compound, which is bluish-green with strong red fluorescence in cold, and becomes a deep-green in hot, glacial acetic acid solution. When heated with methyl-alcoholic potassium hydroxide, phaeophorbin is hydrolysed, yielding chiefly phytochlorin-*e* and phytorhodin-*g* (Willstätter and Hocheder, Abstr., 1907, i, 784).

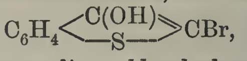
These results confirm the view expressed by previous authors that there are two chlorophylls. Crystalline chlorophyll does not yield phytol, whereas the amorphous compound is a phytol ester. G. Y.

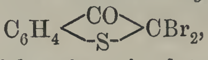
The Chlorophyll Group. LEON MARCHLEWSKI (*Ber.*, 1908, **41**, 453—455).—Phaeophytin (Willstätter and Benz, preceding abstract) is identical with the black precipitate obtained on treating chlorophyll dissolved in 80% alcohol with hydrogen chloride (Schunck and Marchlewski, Abstr., 1894, i, 341). When prepared at the ordinary temperature, it does not contain free phyllocyanin or phylloxanthin, but yields these substances when treated with concentrated hydrochloric acid. Chlorophyllan, which is formed by more energetic action of hydrogen chloride on chlorophyll, contains probably both phyllocyanin and phylloxanthin. G. Y.

Cacao Butter, Especially its Non-hydrolysable Constituents. HERMANN MATTHES and O. ROHDICH (*Ber.*, 1908, **41**, 19—23).—An attempt to isolate the flavouring constituent of cacao butter was not successful. Thirteen kilograms of the butter, after hydrolysis with potassium hydroxide and extraction with ether, gave 28 grams of material which consisted partly of oil and partly of crude phytosterol. The oil, resembling hyacinth in odour, after purification had the following constants: α_D, in 10% benzene, +0·37°; n_D 1·492; iodine number after four and a-half hours, 68·58, and after twenty-four hours, 77·69; and composition C = 80·33, H = 11·77%. The solid consisted of amyrilene, stigmasterol, and phytosterol. The "crude phytosterol" on acetylation gave white leaflets, m. p. 130°, which on bromination gave stigmasterol acetate tetrabromide, of m. p. 180° (decomp.), and phytosterol acetate dibromide, of m. p. 135°. The stigmasterol obtained had m. p. 146°, and phytosterol, m. p. 135—136° [compare Windaus and Hauth, Abstr., 1907, i, 129, who give for stigmasterol, m. p. 170°, and for stigmasterol acetate tetrabromide, m. p. 212° (decomp.)]. W. R.

Derivatives of Thionaphthen. A. Bezdrik, Paul Friedländer, and P. Koeniger (*Ber.*, 1908, 41, 227—242. Compare Abstr., 1906, i, 378; 1907, i, 334).—The definite proof that the compounds previously described contained the thionaphthen complex is now given by the reduction of the synthetical hydroxythionaphthen to thionaphthen. A further series of derivatives has been prepared, of which the products of reaction with the halogens and with nitrous acid demand special attention, substitution here taking place in the thionaphthen nucleus. The action of alkali hydroxides leading to the preparation of thionaphthendicarboxylic acid has also been investigated.

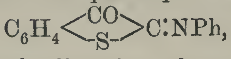
Thionaphthen,  $C_6H_4<\begin{smallmatrix}CH\\S\end{smallmatrix}>CH$, has hitherto been very difficult to prepare in quantity (Gattermann and Lockhardt, Abstr., 1894, i, 92). It is, however, easily obtained by the reduction of hydroxythionaphthen or other thionaphthen derivatives with zinc dust and acetic acid; it has m. p. 221—222°, and forms a crystalline, sparingly soluble mercuriacetate, $C_8H_5S{\cdot}HgC_2H_3O_2$. By means of this, thionaphthen was sought for in the products of tar distillation, but without success.

1-*Bromo-2-hydroxythionaphthen*,  $C_6H_4<\begin{smallmatrix}C(OH)\\S\end{smallmatrix}>CBr$, forms colourless crystals, m. p. 88°; the corresponding *chlorohydroxythionaphthen* is an oil. Both compounds very readily lose hydrogen bromide and form thioindigotin. 1 : 1-*Dibromo-2-ketodihydrothionaphthen*,

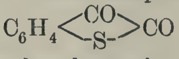


$$C_6H_4<\begin{smallmatrix}CO\\S\end{smallmatrix}>CBr_2,$$

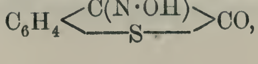
forms brownish-yellow, thick, prismatic plates, m. p. 132°; this is more stable than the monobromide, but gives thioindigotin when heated. It reacts with aniline to form *thionaphthenquinoneanilide*,



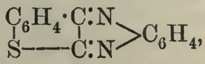
$$C_6H_4<\begin{smallmatrix}CO\\S\end{smallmatrix}>C{:}NPh,$$

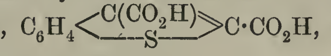
consisting of yellowish-red, glistening plates, m. p. 150—151°. The corresponding p-*toluidide* separates in long, thin, brownish-red needles, m. p. 159°. Both compounds when heated with acids give *thionaphthenquinone*,  $C_6H_4<\begin{smallmatrix}CO\\S\end{smallmatrix}>CO$; this can also be prepared directly from the dibromide by the action of lead acetate, or from 1-nitrosohydroxythionaphthen. It crystallises in well-formed, compact, intensely yellow prisms, m. p. 121°, and distils almost unchanged at 247°. It dissolves in concentrated sulphuric acid with an orange-yellow coloration, and the solution turns intensely blue when shaken with benzene containing thiophen.

Thionaphthenquinone-2-oxime (2-*nitroso*-1-*hydroxythionaphthen*),

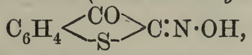


$$C_6H_4<\begin{smallmatrix}C(N{\cdot}OH)\\S\end{smallmatrix}>CO,$$

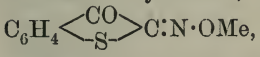
crystallises in long, bright yellow needles, m. p. 186°, and gives rise to an *amino-oxy*-compound which turns red in the air on reduction. The quinone reacts with phenylhydrazine to form the 2-*phenylhydrazone*, of which the orange-yellow crystals have m. p. 165—166°. With *o*-phenylenediamine, a *quinoxaline* derivative,  $\begin{matrix}C_6H_4\cdot C{:}N\\ | \qquad\quad | \\ S\text{———}C{:}N\end{matrix}{>}C_6H_4$, crystallising in colourless needles, m. p. 166—167°, is formed.

Thionaphthenquinone reacts in sodium carbonate solution with chloroacetic acid to form the yellow *sodium* salt of *phenylthioglycollic-o-glyoxalic acid*, $CO_2H\cdot CH_2\cdot S\cdot C_6H_4\cdot CO\cdot CO_2H$, which is converted by sulphuric acid into the free acid; this forms yellow crystals, m. p. 168—169°, gives a yellow *phenylhydrazone*, and forms *o*-carboxyphenylthioglycollic acid when heated with sulphuric acid. Heating with strong alkali hydroxides converts it into *thionaphthen*-1 : 2-*dicarboxylic acid*,  $C_6H_4{<}\begin{matrix}C(CO_2H)\\S\end{matrix}{>}C\cdot CO_2H$, crystallising in small, colourless needles, m. p. 249—251°.

Thionaphthenquinone-1-*oxime* (1-*nitroso*-2-*hydroxythionaphthen*),



$$C_6H_4{<}\begin{matrix}CO\\S\end{matrix}{>}C{:}N\cdot OH,$$

prepared by the action of sodium nitrite on hydroxythionaphthen, crystallises in yellow to brownish-red needles, m. p. 172° (decomp.). It forms a crystalline, orange-yellow *sodium salt* and a *methyl ether*,  $C_6H_4{<}\begin{matrix}CO\\S\end{matrix}{>}C{:}N\cdot OMe$, crystallising in glistening, reddish-yellow needles, m. p. 125°. The *acetate* separates in yellow needles, m. p. 174°; the *benzenesulphonyl* compound likewise forms yellow needles, m. p. 231°.

When reduced in acetic acid solution with zinc dust, nitrosohydroxythionaphthen yields, in the first place, 1-*amino*-2-*hydroxythionaphthen*; this rapidly decomposes, but the *acetate* was obtained in the form of colourless needles, m. p. 189·5°. Both the methyl ether and acetyl derivative of nitrosohydroxythionaphthen yield thiosalicylic acid; when heated with sodium carbonate, however, the acetate gives rise to *o*-thiocyanobenzoic acid, $CNS\cdot C_6H_4\cdot CO_2H$ (Abstr., 1907, i, 335), melting at 166°, and not at 154—155° as stated previously. Alcoholic sodium hydroxide causes the formation of a blue dye, which becomes a dirty red after a time. E. F. A.

Action of Sulphur on Hydrocarbons. GEORGES CAPELLE (*Bull. Soc. chim.*, 1908, [iv], 3, 150—154).—The author proposes to make a general study of the action of sulphur on hydrocarbons.

When acetylene is passed over melted sulphur in the absence of air, hydrogen sulphide, carbon disulphide, and thiophten (Abstr., 1886, 1032) are the principal products. Thiophten crystallises when cooled in a bath of ether and solid carbon dioxide. These compounds seem to be decomposition products of more complex substances first formed in this reaction. T. A. H.

Dibromothiophten. GEORGES CAPELLE (*Bull. Soc. chim.*, 1908, [iv], 3, 154—155).—Thiophten, dissolved in carbon disulphide, reacts with bromine in the same solvent to form *dibromothiophten*, $C_6H_2Br_2S_2$, m. p. 122·5°, which crystallises from alcohol in pearly needles, grouped into tufts, and can be distilled without decomposition. By the prolonged action of bromine on thiophten, Biedermann and Jacobson's tetrabromo-compound is formed (Abstr., 1886, 1032) in addition to a third *bromo*-derivative, m. p. 223°, which may be a polymeride of the tetrabromo-compound. T. A. H.

Double Salts of Alkaloids and Iron. MAX SCHOLTZ (*Ber. deut. pharm. Ges.*, 1908, **18**, 44—52. Compare Christensen, Abstr., 1906, i, 875).—For the purpose of identifying the alkaloids, the complex compounds of the following alkaloid hydrochlorides, with ferric chloride, have been prepared and described. Strychnine forms $C_{21}H_{22}O_2N_2,HCl,FeCl_3$, ruby-red, hexagonal crystals, having no definite m. p. Atropine, $C_{17}H_{23}O_3N,HCl,FeCl_3,H_2O$, pale yellow crystals, m. p. 167—168°. Cocaine, $C_{17}H_{21}O_4N,HCl,FeCl_3$, pale yellow, transparent needles, m. p. 165—166°. Caffeine, $C_8H_{10}O_2N_4,HCl,FeCl_3$, small, canary-yellow, hexagonal crystals, m. p. 77°. Narcotine, $C_{22}H_{23}O_7N,HCl,FeCl_3$, orange, microcrystalline powder, which slowly melts from 75°. Codeine, $C_{18}H_{21}O_3N,HCl,FeCl_3,2H_2O$, minute, yellowish-brown crystals, which slowly melt above 80°. Papaverine, $C_{20}H_{21}O_4N,HCl,FeCl_3,2H_2O$, microscopic, orange grains, m. p. 195°; $C_{20}H_{21}O_4N,HCl,FeCl_3,H_2O$, microscopic, red plates, m. p. 195°. Thebaine, $C_{19}H_{21}O_3N,HCl,FeCl_3,3H_2O$, reddish-brown powder, m. p. 115°. Quinine, $C_{20}H_{24}O_2N_2,2HCl,FeCl_3,H_2O$, small, bright yellow plates, m. p. 170—171°. Cinchonine, $C_{19}H_{22}ON_2,2HCl,FeCl_3,\frac{1}{2}H_2O$, bright yellow, rhombic plates, m. p. 189°. Quinidine, $C_{20}H_{24}O_2N_2,2HCl,FeCl_3,6H_2O$, minute, orange plates, m. p. 220—222°; $C_{20}H_{24}O_2N_2,2HCl,FeCl_3,2H_2O$, dark orange crystals, m. p. 220—222°. Cinchonidine,

$$C_{19}H_{22}ON_2,2HCl,FeCl_3,2H_2O$$

and $C_{19}H_{22}ON_2,2HCl,FeCl_3$, microscopic, brilliant yellow crystals, m. p. 209—210°. From coniine and theobromine, no salt could be obtained; nicotine gave an oil, and brucine a dark flocculent precipitate. J. V. E.

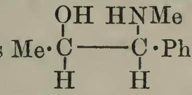
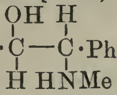
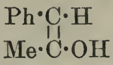
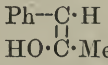
Arecaidine and Arecoline. HANS MEYER (*Ber.*, 1908, **41**, 131).—A claim for priority over Wohl and Johnson (this vol., i, 49), who have overlooked the previous determination of the formulæ of these alkaloids (Abstr., 1902, i, 390). E. F. A.

Cheiroline, an Alkaloid containing Sulphur. PH. WAGNER (*Chem. Zeit.*, 1908, **32**, 76—77. Compare Reeb, Abstr., 1900, i, 186).—*Cheiroline*, $C_9H_{16}O_7N_2S_2$, is obtained by extracting with ether powdered wallflower seeds moistened with 5% sodium carbonate solution, and shaking the ethereal extract with 5% sulphuric acid. The filtered acid solution is rendered alkaline with sodium carbonate and extracted with ether; the alkaloid separates from the ethereal solution on evaporation. It crystallises in colourless prisms, m. p. 46—48°, and is similar to quinine in its physiological action. When warmed with water and mercuric oxide, it yields *cheirole*, $C_9H_{20}O_9N_2$, crystallising in colourless needles, m. p. 172·5°. W. H. G.

Ephedrine and ψ-Ephedrine, a case of Asymmetry due to Dissimilar Halves. Hermann Emde (*Arch. Pharm.*, 1907, 245, 662—679).—The author agrees with Fourneau's conclusion (Abstr., 1907, i, 762) that the quaternary base obtained by Schmidt and Emde from cinnamyltrimethylamine hydrochloride (Abstr., 1906, i, 946) is benzyldimethylaminomethylcarbinol, and has the constitution

$$OH\cdot CH(CH_2Ph)\cdot CH_2\cdot NMe_3\cdot OH,$$

and not $OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot NMe_3\cdot OH$ as supposed by these authors; the addition of hypochlorous acid here takes place in the opposite way to that in which it unites with cinnamic acid. The aurichloride of the quaternary base described by Schmidt and Flaecher (Abstr., 1905, i, 371) does not melt at 170°, as erroneously stated, but at 150—151°, and is thus identical with the aurichloride of the base prepared by means of hypochlorous acid by Schmidt and Emde.

After various speculations, the author concludes that ephedrine and ψ-ephedrine are not structural, but optical, isomerides of the configurations  $Me\cdot\overset{OH}{\underset{H}{C}}\text{——}\overset{HNMe}{\underset{H}{C}}\cdot Ph$ and  $Me\cdot\overset{OH}{\underset{H}{C}}\text{—}\overset{H}{\underset{HNMe}{C}}\cdot Ph$ respectively. The isomerism would therefore resemble that existing between *l*-arabonic and *l*-ribonic acids, for instance. In the same way that these acids are mutually convertible by heating with pyridine, the two ephedrines can be transformed into each other by heating with hydrochloric acid, for, as Schmidt has found, the change from ephedrine to ψ-ephedrine is reversible. The two alcohols which are formed from the bases by Hofmann's degradation would, on this view, be the two stereoisomeric forms of 1-phenylpropenol,  $\begin{matrix}Ph\cdot C\cdot H\\ \|\\ Me\cdot C\cdot OH\end{matrix}$ and  $\begin{matrix}Ph\text{—}C\cdot H\\ \|\\ HO\cdot C\cdot Me\end{matrix}$.

By repeated distillation, the boiling point of the alcohol from ψ-ephedrine (197—199°) is raised to that of the alcohol from ephedrine (212—216°), so that these alcohols are convertible.

The chief reason why the methylimide group in ephedrine and ψ-ephedrine is regarded as attached to the carbon atom adjoining the benzene ring, is the ease with which the carbon-nitrogen linking is broken down by Hofmann's reaction. This linking is regarded as being rendered less stable by the double bonds of the benzene nucleus, in the same way that the group $N\cdot C\colon C$ is unstable in tetrahydropicoline and other bases having a double bond adjoining the nitrogen atom. But for this consideration, ephedrine and ψ-ephedrine might equally well be represented by the formula $OH\cdot CHPh\cdot CHMe\cdot NHMe$, previously suggested by Fourneau and by Emde for one or other of the two isomerides. G. B.

Crystalline Hydroergotinine Sulphate. Friedrich Kraft (*Arch. Pharm.*, 1907, 245, 644—645. Compare Abstr., 1906, i, 979).—The preparation, by Barger and Carr (Trans., 1907, 91, 337), of crystalline salts of the amorphous ergot alkaloid ergotoxine (hydroergotinine) has now enabled the author to crystallise the sulphate, which hitherto he had only obtained amorphous.

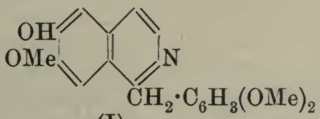
Hydroergotinine sulphate forms flat, rhombic prisms, from 95% alcohol, of the composition $(C_{35}H_{41}O_6N_5)_2,H_2SO_4$, confirming the formula $C_{35}H_{41}O_6N_5$ assigned to ergotoxine by Barger and Carr. It was found impossible to prepare a crystalline sulphate from ergotinine; the two ergot alkaloids are distinct, notwithstanding Tanret's view that they are identical. G. B.

Ergotoxine and other Constituents of Ergot. George Barger and Henry H. Dale (*Bio-Chem., J.*, 1907, **2**, 240—299. Compare Abstr., 1907, i, 79).—The alkaloid ergotoxine isolated by Barger and Carr (Trans., 1907, **91**, 337) produces in very small doses the effects hitherto described as characteristic of ergot, including gangrene. Ergotinine is but slightly, if at all, active when pure. The relation of Kobert's cornutine and sphacelinic acid and of Jacobj's preparations to ergotoxine is discussed; the richest in ergotoxine seems to have been Jacobj's sphacelotoxine, which probably contained something like 40%. A list of synonyms of "active principles" is given. Vahlen's clavine (Abstr., 1906, i, 876) is a mixture of leucine and aspartic acid, and was accordingly found to be physiologically inactive. G. B.

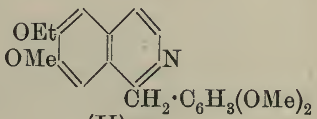
Action of Free Alkalis on Morphine and Adrenaline. A Contribution to Sterilisation. M. Grübler (*Chem. Zentr.*, 1907, ii, 1424; from *Pharm. Post.*, 1907, **40**, 579—582).—As free alkali may be formed by the action of hot water on glass apparatus during sterilisation, it is recommended to test glass for use with alkaloid salts by heating with phenolphthalein in boiling water or in the steam current of a steriliser for half-an-hour, and to reject all glass giving a red coloration. Free alkali from glass gives a yellow coloration with morphine salts, ψ-morphine being formed in proportion to the amount of the free alkali. Hence morphine salts may serve to indicate the quality of a glass.

Adrenaline can be sterilised only if the glass does not yield free alkali; the sensitiveness of this alkaloid is shown by adding one drop of *N*-sodium hydroxide to 0·5 c.c. of a 1 : 3000 adrenaline solution, when an intense red coloration is obtained; this changes slowly to yellow, but again appears when the mixture is shaken with air. This reaction is visible with even smaller quantities of adrenaline, and is also given by suprarenine, paranephrine, and epirenan. G. Y.

Phenolbetaines from Papaverine. Herman Decker and Georges Dunant (*Annalen*, 1908, **358**, 288—326).—Decker and Klauser (Abstr., 1904, i, 338) found that the action of alkalis on papaverinium alkyl haloids leads to the formation of *iso*papaverine bases, which, on oxidation in alkaline solution, yield dimethoxy-*N*-alkyl*iso*quinolones and veratric acid. Hence Goldschmiedt and Stransky's supposed methyl- and ethyl-papaverinium hydroxides (Abstr., 1889, 166; 1890, 179) were considered to have been formed from impure *iso*papaverine bases. A re-investigation has shown, however, that the action of alkalis on papaverinium alkyl haloids takes place in three ways, depending on the conditions: (1) with very dilute alkalis, the papaverinium hydroxides are liberated, and undergo gradual condensation to phenolbetaines (Griess, Abstr., 1880, 636, 637); (2) with concentrated alkalis, the quaternary hydroxides are transformed into the isomeric carbinols, which lose water, forming *iso*papaverine bases, and then, in consequence of oxidation by the air, *iso*quinolones and veratraldehyde. The aldehyde is converted by the alkali into veratryl alcohol and veratric acid, and (3) with alcoholic alkalis, alkylamines are formed together with a phenol, which must result from a far-reaching change in the papaverine nucleus. The constitution of this phenol remains unexplained. Goldschmiedt and Stransky's supposed papaverinium salts were, for at least the most part, salts of phenolbetaines. The terms "norpapaverine" (I) and "homopapaverine" (II) are proposed; the positions of the methoxy- and hydroxy-groups in the former, and the methoxy- and ethoxy-groups in the latter, may be interchanged:

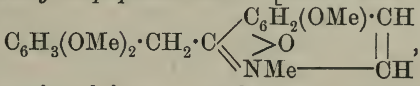


(I)



(II)

In the following description of the compounds obtained, the m. p.'s in brackets are those given by Goldschmiedt and Stransky.

Derivatives of N-*Methylnorpapaverinium.*—[With MAX GIRARD.]—The phenolbetaine,  $C_6H_3(OMe)_2{\cdot}CH_2{\cdot}C\begin{cases} C_6H_2(OMe){\cdot}CH \\ >O \qquad\quad || \\ NMe{-}{-}{-}{-}CH \end{cases}$, from *N*-methylpapaverinium methosulphate, crystallises in cubes ($6-7H_2O$), m. p. 60—65°, or, when dried and crystallised from chloroform, yellow crystals, m. p. 251° (215°) (partial decomp.), gives a blue coloration with concentrated sulphuric acid, and when heated with hydriodic acid yields *N*-methylpapaveroline, m. p. 232°. The picrate, $C_{26}H_{24}O_{11}N_4$, m. p. 215° (205°); the *hydrochloride* (*norpapaverine methochloride*), $C_{20}H_{22}O_4NCl$, colourless crystals, m. p. 222°; the platinichloride and hydrogen chromate, $C_{20}H_{22}O_4N,HCrO_4$, were analysed; the *mercurichloride* forms colourless crystals. Norpapaverine methiodide, yellow crystals (H_2O), m. p. 100°, or, when dried, 180° (decomp.).

Derivatives of N-*Ethylnorpapaverinium.*—The phenolbetaine, $C_{21}H_{23}O_4N,6H_2O$, yellow crystals, m. p. 66—67° (72°), or, when anhydrous, 179—180° (175—180°); the hydrochloride (norpapaverine ethochloride), crystals ($4-5H_2O$), m. p. below 100° (80°), or, when anhydrous, 196°; the *hydrobromide*, $C_{21}H_{24}O_4NBr,4H_2O$, m. p. 61—62°, or, when anhydrous, 195—196°; the picrate, m. p. 179—180° (175°); the *dichromate* forms reddish-brown, unstable crystals; the *hydriodide*, yellow crystals, melting in water below 100°.

Derivatives of N-*Methylhomopapaverinium.*—*Homopapaverine meth-*

iodide, $C_{21}H_{23}O_4NMeI,C_2H_6O$, forms orange, crystalline masses, loses C_2H_6O at 100°, m. p. 187—188° (decomp.); the *picrate*,

$$C_{21}H_{23}O_4NMe\cdot C_6H_2O(NO_2)_3,$$

yellow needles, m. p. 133—134°. The *methobromide*, on treatment with concentrated sodium hydroxide, yields the yellow iso*homopapaverine* base, $C_{21}H_{22}O_4NMe$, which is decomposed by nitric acid, D 1·3, forming a *substance*, crystallising in white needles, m. p. 192°, nitrohomoveratrole, m. p. 117°, and *methoxyethoxy*-N-*methyl*iso*quinolone*, m. p. 120—123°; *hydrochloride*, m. p. 86°, or, when anhydrous, 189°, decomp. 191° (compare Pschorr, Abstr., 1904, i, 611).

Derivatives of N-*Ethylhomopapaverinium.*—The *iodide* (*homopapaverine ethiodide*), $C_{23}H_{28}O_4NI$, m. p. 221—223° (decomp.); the *picrate*, $C_{29}H_{30}O_{11}N_4$, yellow crystals, m. p. 126—127° (decomp.). The iso*base* forms a yellow, crystalline mass, which, on treatment successively with concentrated nitric acid and an alkali, yields nitrohomoveratrole and *methoxyethoxy*-N-*ethyl*iso*quinolone.*

The following facts as to the quaternary salts of papaverine are new: they differ from the salts of the phenolbetaines in that they do not give precipitates with ammonia and sodium carbonate. *N*-Methylpapaverinium picrate (Decker and Klauser, *loc. cit.*) melts at 132—133°, resolidifies, and again melts at 175—176°; the *methosulphate*, $C_{20}H_{21}O_4NMe\cdot SO_4Me$, is crystalline; the methiodide, m. p. 60—65°, or, when anhydrous, 195° (decomp.). The salts are obtained from the phenolbetaine of *N*-methylnorpapaverinium by the action of methyl sulphate and methyl iodide respectively. The quaternary salts of *N*-ethylpapaverine are formed in the same manner from the phenolbetaine of *N*-ethylnorpapaverinium.

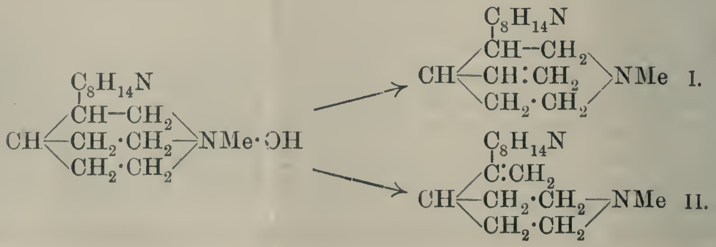
When boiled with alcoholic potassium hydroxide, papaverinium methiodide yields methylamine and a phenol-like *substance*,

$$C_{16}H_8O(OMe)_4 ?,$$

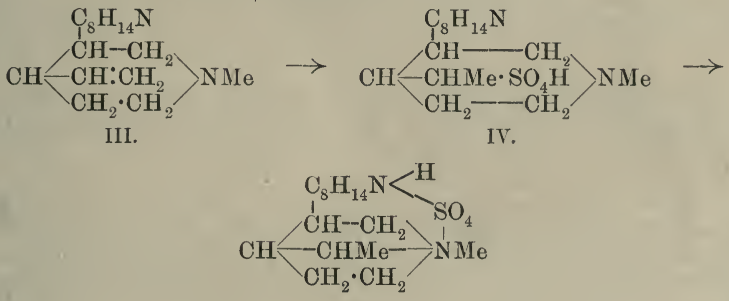
which crystallises in needles, m. p. 180°, and forms *acetyl*, *benzoyl*, and *methyl* derivatives. G. Y.

Constitution of α- and β-Methylsparteine and of *iso*Sparteine.

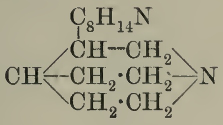
CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1908, **146**, 79—82. Compare this vol., i, 43, 44, 103).—Accepting the constitutional formula for sparteine suggested by the authors (Abstr., 1905, i, 659, 717), the formation of two isomeric methylsparteines by the decomposition of α-methylsparteinium hydroxide (this vol., i, 44) is readily explained according to the following scheme:

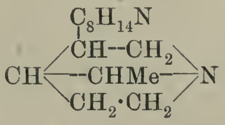


It is not possible at this stage to decide which of these formulæ represents the constitution of α-methylsparteine, but the formation of *iso*sparteine derivatives from α-methylsparteine salts is readily explained assuming α-methylsparteine has the constitution I, and the following scheme represents the isomeric changes whereby α-methylsparteine sulphate is converted into *iso*sparteine methosulphate :


III. IV. V.

These changes involve the closing of the piperidine ring that was opened by the decomposition of the α-methylsparteinium hydroxide to form a pyrrolidine ring, and *iso*sparteine (VII) may be regarded as derived from sparteine (VI) by the conversion of a piperidine into a pyrrolidine ring :

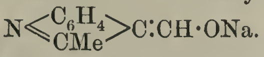

VI.


VII.

M. A. W.

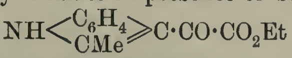
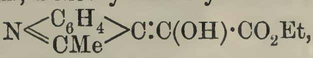
New Reactions of Indoles and Pyrroles. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 790—795).—The authors describe products obtained by the condensation of 2-methylindole with various carboxylic esters in presence of sodium alkoxide or sodium.

2-Methylindole and amyl formate in presence of sodium amyloxide or sodium yield the sodium derivative of 2-methylindole-3-aldehyde,

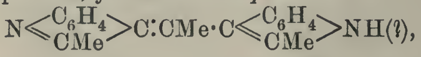


$$N{<}\begin{matrix}C_6H_4\\CMe\end{matrix}{>}C{:}CH{\cdot}ONa.$$

2 : 2-Dimethylindole reacts with amyl formate giving a compound, the p-*nitrophenylhydrazone*, $C_{13}H_{14}O_2N_4$, of which crystallises from acetone or alcohol in red needles, m. p. 210°.

With ethyl oxalate in presence of sodium, 2-methylindole yields the *compound*,  $NH{<}\begin{matrix}C_6H_4\\CMe\end{matrix}{>}C{\cdot}CO{\cdot}CO_2Et$ or  $N{<}\begin{matrix}C_6H_4\\CMe\end{matrix}{>}C{:}C(OH){\cdot}CO_2Et$, which crystallises from benzene in yellow needles, m. p. 126°. The corresponding carboxylic *acid*, $C_{11}H_9O_3N$, dissolves readily in alcohol or acetone, decomposes at about 190°, and when boiled with dilute sulphuric acid gives an intense magenta coloration.

The interaction of 2-methylindole, ethyl acetate, and sodium ethoxide in molecular proportion, yields the *compound*



$$N\left\langle\begin{matrix}C_6H_4\\CMe\end{matrix}\right\rangle C{:}CMe\cdot C\left\langle\begin{matrix}C_6H_4\\CMe\end{matrix}\right\rangle NH(?),$$

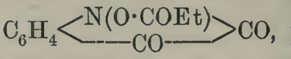
which separates from benzene in shining crystals, m. p. 203°.
T. H. P.

[4-Methylisatin.] Rudolph Bauer (*Ber.*, 1908, **41**, 450).—4-*p*-Methylisatin has m. p. 187°, not 155° as was incorrectly stated (Abstr., 1907, i, 603).
C. S.

A New Step in the Reduction of the Nitro-group. II. Gustav Heller and Apostolos Sourlis (*Ber.*, 1908, **41**, 373—378).—Further details as to the first product of the reduction of the nitro-group. The properties of Bamberger's agnotobenzaldehyde (Abstr., 1907, i, 163) show it to be a molecular compound of *o*-nitrobenzaldehyde and *o*-hydroxylaminobenzaldehyde, and not a derivative of a dihydroxylamino-compound.

The *compound*,

$$N(OH)_2\cdot C_6H_4\cdot CH(OH)\cdot CN,OH\cdot NH\cdot C_6H_4\cdot CH(OH)\cdot CN,$$

previously isolated as the hydrochloride, forms colourless crystals, m. p. 180° (decomp.). When treated with phenylhydrazine in acetic acid solution, it yields 1-hydroxyisatinphenylhydrazone and the α- and β-phenylhydrazones of isatin. The hydrochloride of the double compound is decomposed by water, forming a *substance*, $C_{16}H_{13}O_5N_3$, decomp. 175°, and small amounts of isatin or anthroxanic acid, which are formed also by the action of hydrochloric acid on the main product; this is considered to be a molecular compound of isatin and dihydroxylaminomandelonitrile. The action of aqueous potassium hydroxide on the hydrochloride leads to the formation of dibenzoyldioxindol. 1-*Propionoxyisatin*,  $C_6H_4\left\langle\begin{matrix}N(O\cdot COEt)\\CO\end{matrix}\right\rangle CO$, prepared by heating the hydrochloride with propionic anhydride, forms orange-yellow crystals, m. p. 105—106°, and behaves towards alkalis and phenylhydrazine in the same manner as the *l*-acetoxy-compound (*loc. cit.*).
G. Y.

Preparation of a Hydroxyquinolinesulphonic Acid. Franz Fritzsche & Co. (D.R.-P. 187869).—A new 8-*hydroxyquinolinesulphonic acid*, m. p. 310—313°, produced by heating 8-hydroxyquinoline and concentrated sulphuric acid at 90° for about three days, is a lemon-yellow, crystalline powder, sparingly soluble in water and alcohol. Its *potassium* and *sodium* salts are soluble; they crystallise respectively in leaflets and needles. Its *barium*, *iron*, *silver*, *zinc*, and *bismuth* salts are described. Both the acid and its salts have useful therapeutic properties.
G. T. M.

[Condensation of the Arylsulphonyl-α-naphthylamines with *p*-Aminophenols.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 187823).—*p*-Toluenesulphonyl-α-naphthylamine, when oxidised with alkaline hypochlorite solution in the presence of *p*-aminophenol, furnishes an *indophenol*, $O:C_6H_4:N\cdot C_{10}H_6\cdot NH\cdot SO_2\cdot C_7H_7$, and this product or the corresponding leucoindophenol, when heated at 120° with sulphur, crystallised sodium sulphide, and copper sulphate or copper powder yields a sparingly soluble, greenish-black dye, which gives very fast shades of green on cotton. G. T. M.

Action of Diazo-chlorides on α- and γ-Bromoacetoacetic Esters. G. FAVREL (*Bull. Soc. chim.*, 1907, [iv], 1, 1238—1241).—It has been shown previously (compare Abstr., 1907, i, 796) that the α- and γ-chloroacetoacetates may be readily distinguished by their action on diazo-chlorides; thus ethyl α-chloroacetoacetate yields with diazobenzene chloride, ethyl chloroglyoxylate-phenylhydrazone, whereas the γ-ester furnishes ethyl γ-chloro-αβ-diketobutyrate-phenylhydrazone and, finally, ethyl diphenylformazylformate (Abstr., 1902, i, 644; 1907, i, 796). It is now shown that the corresponding bromo-esters both behave in the same way with diazo-chlorides.

On adding ethyl γ-bromoacetoacetate to diazobenzene chloride, *ethyl γ-bromo-αβ-diketobutyrate-α-phenylhydrazone*,

$$CH_2Br\cdot CO\cdot C(N_2HPh)\cdot CO_2Et,$$

m. p. 78—80°, crystallising in yellow needles, is formed together with some ethyl diphenylformazylformate. The corresponding α-o-*tolylhydrazone*, m. p. 108—110°, crystallises from alcohol, and the isomeric p-*compound* melts at 82—83°. The *methyl* esters, corresponding with the first two substances described, are crystalline, and melt at 104—105° and 139—140° respectively.

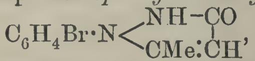
Ethyl α-bromoacetoacetate is very unstable; at temperatures above 0°, it readily passes into the γ-isomeride, and gives with diazo-chlorides the same compounds as the latter. In brominating ethyl acetoacetate at −15 to −20°, ethyl γγ-dibromoacetoacetate is formed. T. A. H.

3-Pyrazolones. III. AUGUST MICHAELIS (*Annalen*, 1907, **358**, 127—170. Compare Abstr., 1905, i, 377; 1907, i, 154).—In continuation of the study of the 3-pyrazolones, 1-*p*-bromophenyl- and 1-*m*-nitrophenyl-5-methyl-3-pyrazolones and 1 : 5-diphenyl-3-pyrazolone and a number of their derivatives have been prepared and are now described. The bromo-compound resembles 1-phenyl-5-methyl-3-pyrazolone, forming a green nitroso-derivative, a red benzeneazo-compound, a stable 4-amino-derivative, and a 4-azopyrazolone, which crystallises more readily than the azophenylmethyl-3-pyrazolone. 1-*m*-Nitrophenyl-5-methyl-3-pyrazolone, on the other hand, does not form either a nitroso- or a benzeneazo-derivative, but is comparatively easily converted into 1-*m*-nitroantipyrine; it does not combine directly with methyl iodide, but the methiodide, from which the 3-thiopyrine is readily formed, is obtained by successive treatment of the pyrazolone with methyl sulphate and potassium iodide.

1 : 5-Diphenyl-3-pyrazolone (Knorr and Klotz, Abstr., 1887, 1121), obtained in good yields by condensation of acetylphenylhydrazide with

ethyl benzoylacetate in presence of phosphorus trichloride, in its reactions resembles 1-*m*-nitrophenyl-5-methyl-3-pyrazolone.

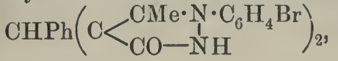
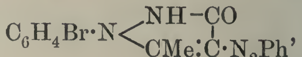
1. 1-p-*Bromophenyl-* and 1-*m-Nitrophenyl-5-methyl-3-pyrazolone.*—[With A. Stiegler.]—1-p-*Bromophenyl-5-methyl-3-pyrazolone,*



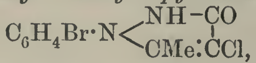
$$C_6H_4Br\cdot N{<}\begin{matrix}NH-CO\\ CMe{:}CH\end{matrix},$$

prepared by heating acetyl-*p*-bromophenylhydrazide with ethyl acetoacetate and phosphorus trichloride at 45° and, finally, at 70°, separates from alcohol in white crystals, m. p. 227°, and is soluble in acids and alkalis. The *hydrochloride*, $C_{10}H_9ON_2Br,HCl$, crystallises in white needles, m. p. 200°, and is decomposed by water; the *sodium* salt, $C_{10}H_8ON_2BrNa$, was analysed. The *benzenesulphonate*,

$$C_6H_4Br\cdot C_3N_2HMe\cdot O\cdot SO_2Ph,$$

forms white crystals, m. p. 96°; the benzoate, $C_{10}H_8ON_2BrBz$, crystallises in white needles, m. p. 86°. The 4-*benzylidene* derivative,  $CHPh\left(C{<}\begin{matrix}CMe\cdot N\cdot C_6H_4Br\\ CO-NH\end{matrix}\right)_2$, forms a white, crystalline powder, m. p. 273°. The 4-*benzeneazo*-derivative,  $C_6H_4Br\cdot N{<}\begin{matrix}NH-CO\\ CMe{:}C\cdot N_2Ph\end{matrix}$, crystallises in red prisms, m. p. 219°.

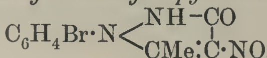
4-*Chloro*-1-p-*bromophenyl-5-methyl-3-pyrazolone,*



$$C_6H_4Br\cdot N{<}\begin{matrix}NH-CO\\ CMe{:}CCl\end{matrix},$$

prepared by heating the pyrazolone with phosphorus pentachloride at 150°, separates from alcohol in small, white crystals, m. p. 220°. The corresponding 4-*bromo*-compound, $C_{10}H_8ON_2Br_2$, forms colourless crystals, m. p. 231°. The 4-*iodo*-compound, prepared by treating the pyrazolone successively with mercuric chloride in hot saturated solution and an excess of iodine, crystallises in yellow leaflets, m. p. 207° (decomp.).

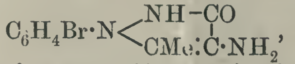
4-*Nitroso*-1-p-*bromophenyl-5-methyl-3-pyrazolone,*



$$C_6H_4Br\cdot N{<}\begin{matrix}NH-CO\\ CMe{:}C\cdot NO\end{matrix},$$

prepared by treating the 3-pyrazolone with nitrogen trioxide in cooled glacial acetic acid solution, crystallises in emerald-green needles, becoming brown at 180°, m. p. 185°, dissolves unchanged in alkalis and acids, and gives Liebermann's reaction; the *hydrochloride*, $C_{10}H_8ON_2Br\cdot NO,HCl$, crystallises in yellow needles, m. p. 210°, and is stable towards cold water. The 4-*nitro*-derivative,

$$C_{10}H_8ON_2Br\cdot NO_2,$$

obtained on heating the pyrazolone with concentrated nitric acid, crystallises in white needles, m. p. 211·5°, and forms yellow solutions in alkalis. Reduction of the nitro- or nitroso-compound with zinc and acetic acid leads to the formation of 4-*amino*-1-p-*bromophenyl-5-methyl-3-pyrazolone,*  $C_6H_4Br\cdot N{<}\begin{matrix}NH-CO\\ CMe{:}C\cdot NH_2\end{matrix}$, which, after purification by conversion into its benzylidene derivative and hydrolysis of this with an alkali, separates from chloroform in white crystals, m. p. 238°, is stable when dry, but readily becomes brown on exposure to moist air, reduces Fehling's solution in the cold or ammoniacal silver solutions when heated, and gives a characteristic, reddish-brown coloration with calcium hypochlorite. The *hydrochloride*, $C_{10}H_8ON_2Br\cdot NH_2,HCl$, forms white crystals, m. p. 291°; the *picrate*, $C_{10}H_{10}ON_3Br,C_6H_3O_7N_3$, crystallises from alcohol in brownish-yellow needles, m. p. 200°. The *benzylidene* derivative, $C_{10}H_8ON_2Br\cdot N{:}CHPh$, separates from ethyl acetate in white crystals, m. p. 249°, and becomes brown on exposure to air; the m-*nitrobenzylidene* derivative, yellow crystals, m. p. 274°; the *anisylidene* derivative, yellow plates, m. p. 303°. The base condenses with Michler's ketone, forming the *product*,

$$C_{10}H_8ON_2Br\cdot N{:}C(C_6H_4\cdot NMe_2)_2,$$

crystallising in silvery leaflets, m. p. 330°, and with ethyl acetoacetate, forming the *product*, $C_{10}H_8ON_2Br\cdot N{:}CMe\cdot CH_2\cdot CO_2Et$, crystallising in white needles, m. p. 199°. The 4-*thionylamino*-compound,

$$C_{10}H_8ON_2Br\cdot N{:}SO,$$

obtained by treating the amine with thionyl chloride in hot benzene solution, crystallises in yellow needles, m. p. 168°, decomposes on exposure to moist air, and yields a sulphite and the amino-pyrazolone when treated with an alkali. The *acetyl* derivative, $C_{10}H_8ON_2Br\cdot NHAc$, forms white crystals, m. p. 259°; the *formyl* derivative is obtained as a crystalline powder, m. p. 240°; the *dibenzoyl* derivative,

$$OBz\cdot C_{10}H_7N_2Br\cdot NHBz,$$

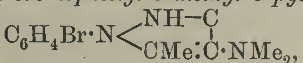
crystallises from alcohol in white needles, m. p. 188°. The 4-*carbamido*-compound, $C_{10}H_8ON_2Br\cdot NH\cdot CO\cdot NH_2$, forms white crystals, does not melt at 350°, and is readily soluble in aqueous alkalis; 4-*phenylthiocarbamido*-1-p-*bromophenyl*-5-*methyl*-3-*pyrazolone*,

$$C_{10}H_8ON_2Br\cdot NH\cdot CS\cdot NHPh,$$

crystallises in white prisms, m. p. 262°, and is decomposed by hot acids; the s-*thiocarbamide*, $CS(NH\cdot C_{10}H_8ON_2Br)_2$, prepared by heating the 4-amino-pyrazolone with carbon disulphide on the water-bath, forms a yellow, crystalline powder, m. p. 289°. The *diazo-chloride*, $C_{10}H_8ON_2Br\cdot N_2Cl$, prepared by the action of sodium nitrite on the amine hydrochloride, forms a light yellow, gelatinous mass, remains unchanged when evaporated with water, is soluble in chloroform, and in aqueous solution couples with amines and phenols; the *dye*, $C_{10}H_8ON_2Br\cdot N_2\cdot C_{10}H_6\cdot OH$, formed by coupling the diazo-chloride with β-naphthol, crystallises in orange-red needles, m. p. 253°. Similar *dyes* are obtained from salicylic acid, resorcinol, aniline, and dimethylaniline.

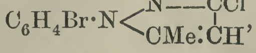
4-*Azo*-1-p-*bromophenyl*-5-*methyl*-3-*pyrazolone*, $N_2(C_{10}H_8ON_2Br)_2$, prepared by coupling the diazo-chloride with the pyrazolone in alkaline solution, crystallises in reddish-brown needles, m. p. 175°.

4-*Dimethylamino*-1-p-*bromophenyl*-5-*methyl*-3-*pyrazolone*,



$$C_6H_4Br\cdot N{<}\begin{array}{l}NH{-}C\\ \qquad\quad\vert\\ CMe{:}C\cdot NMe_2\end{array},$$

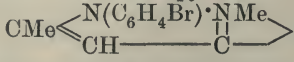
prepared by heating the amino-pyrazolone with methyl iodide and potassium hydroxide in methyl-alcoholic solution, forms refracting, yellow crystals, m. p. 190°.

3-*Chloro*-1-p-*bromophenyl*-5-*methylpyrazole*,  $C_6H_4Br\cdot N{<}\begin{array}{l}N{=\!=}CCl\\ \qquad\vert\\ CMe{:}CH\end{array}$,

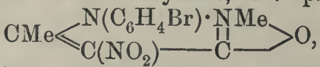
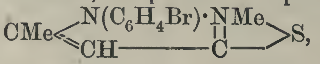
formed by heating the 3-pyrazolone with phosphoryl chloride at 210°, is obtained as a colourless oil, which gradually solidifies, m. p. 45°, b. p. 200°/15 mm. or 211°/30 mm. The *methiodide*,

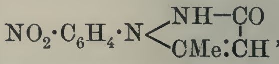
$C_{10}H_8N_2ClBr,MeI$,

prepared by heating the chloropyrazole with methyl iodide at 100—115°, crystallises in white prisms, m. p. 207°. 4-*Azo-3-chloro*-1-p-*bromophenyl-5-methylpyrazole*, $N_2(C_{10}H_7N_2ClBr)_2$, formed by heating 4-azobromophenylmethylpyrazolone with phosphoryl chloride at 125°, crystallises in yellow needles, m. p. 203°, sublimes when highly heated, and cannot be reduced to the azopyrazole.

3-p-*Bromoantipyrine*,  $\mathrm{CMe}<\begin{array}{l}\mathrm{N(C_6H_4Br)\cdot NMe}\\ \mathrm{CH{-}{-}{-}{-}{-}C}\end{array}>\mathrm{O}$, is formed by the action of alkalis on 1-*p*-bromophenyl-5-methyl-3-pyrazolone methiodide, or by heating the 3-pyrazolone with methyl iodide and methyl alcohol in a sealed tube at 115°, but is best prepared by heating the 3-pyrazolone with methyl sulphate and treating the product with an alkali. It crystallises from chloroform in white prisms, m. p. 150°, distils almost unchanged in a vacuum, gives with ferric chloride a red, with fuming nitric acid a green, coloration becoming reddish-yellow, and does not yield a nitroso-derivative. The *hydrochloride*, $C_{11}H_{11}ON_2Br,HCl$, m. p. 225°; the *picrate*, $C_{11}H_{11}ON_2Br,C_6H_3O_7N_3$, m. p. 169°; the *ferrocyanide*, $(C_{11}H_{11}ON_2Br)_2,H_4Fe(CN)_6$, forms a white, crystalline precipitate, decomp. about 310°. The action of bromine on 3-bromoantipyrine leads to the formation of 4-*bromo*-1-p-*bromophenyl*-3 : 5-*dimethylpyrazolone* ("4′ : 4-*dibromo-3-antipyrine*"),

$C_6H_4Br\cdot C_3N_2OBrMe_2$

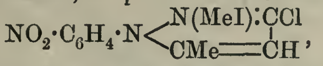
which forms white crystals, m. p. 163°. 4-*Nitro*-1-p-*bromo*-3-*antipyrine*,  $\mathrm{CMe}<\begin{array}{l}\mathrm{N(C_6H_4Br)\cdot NMe}\\ \mathrm{C(NO_2){-}{-}{-}C}\end{array}>\mathrm{O}$, formed by the action of sodium nitrite on the antipyrine in glacial acetic acid solution, crystallises in yellow needles, m. p. 221°. 1-p-*Bromophenyl*-3:5-*dimethyl*-3-*thiopyrazolone*,  $\mathrm{CMe}<\begin{array}{l}\mathrm{N(C_6H_4Br)\cdot NMe}\\ \mathrm{CH{-}{-}{-}{-}{-}C}\end{array}>\mathrm{S}$, prepared by the action of potassium hydrogen sulphide on 3-chloro-1-*p*-bromophenyl-5-methylpyrazole methiodide in alcoholic solution, crystallises in yellow needles, m. p. 236°, and gives an intense yellow coloration with sulphurous acid.

1-m-*Nitrophenyl-5-methyl-3-pyrazolone*,  $\mathrm{NO_2\cdot C_6H_4\cdot N}<\begin{array}{l}\mathrm{NH{-}CO}\\ \mathrm{CMe{:}CH}\end{array}$, prepared by condensation of acetyl-*m*-nitrophenylhydrazide with ethyl acetoacetate in presence of phosphorus trichloride, separates from alcohol in almost white crystals, m. p. 239°, is soluble in acids, and forms yellow solutions in alkalis. The *hydrochloride*,

$C_{10}H_9ON_2\cdot NO_2,HCl$,

yellow crystals, m. p. 235°; the *sodium* salt, $C_{10}H_8O_3N_3Na$, yellow needles. The *benzenesulphonate*, $NO_2\cdot C_{10}H_8ON_2\cdot SO_2Ph$, golden leaflets, m. p. 90°; the *benzoate*, $NO_2\cdot C_{10}H_8ON_2Bz$, white needles, m. p. 130°. The *benzylidene* derivative, $CHPh(C_{10}H_8ON_2\cdot NO_2)_2$, a white, crystalline powder, m. p. 197°. The 4-*chloro*-, m. p. 253°, 4-*bromo*-, m. p. 245°, and 4-*iodo*-, m. p. 221°, derivatives were analysed.

3-*Chloro*-1-m-*nitrophenyl*-5-*methylpyrazole*, $NO_2\cdot C_6H_4\cdot C_3N_2HClMe$, prepared by heating the pyrazolone with phosphoryl chloride at 190°, crystallises in white leaflets, m. p. 135°. The *methiodide*,



$$NO_2\cdot C_6H_4\cdot N<\begin{matrix}N(MeI)\colon CCl \\ CMe{=\!=}CH\end{matrix},$$

prepared by way of the methosulphate, forms yellow crystals, m. p. 196·5°.

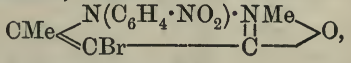
3-*Chloro*-1-m-*aminophenyl*-5-*methylpyrazole*, $NH_2\cdot C_6H_4\cdot C_3N_2HClMe$, is formed by reduction of the nitrophenylpyrazole with tin and hydrochloric acid; it crystallises in white needles, m. p. 94°. The *hydrochloride*, $C_{10}H_8N_2Cl\cdot NH_2,HCl$, crystallises in needles, m. p. 103°.

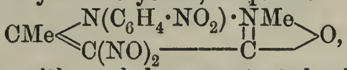
1-m-*Nitro*-3-*antipyrine*, $NO_2\cdot C_6H_4\cdot C_3N_2OHMe$, prepared by heating 1-*m*-nitrophenyl-5-methyl-3-pyrazolone with methyl iodide at 115° and treating the product with sodium hydroxide, or by heating the pyrazolone with methyl sulphate, forms yellow crystals, m. p. 181°, and behaves towards ferric chloride and fuming nitric acid in the same manner as 1-*p*-bromo-3-antipyrine. The *picrate*,

$$C_{11}H_{11}ON_2\cdot NO_2,C_6H_3O_7N_3,$$

yellow prisms, m. p. 149°; the *ferrocyanide*,

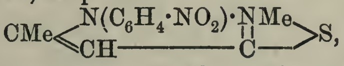
$$(C_{11}H_{11}ON_2\cdot NO_2)_2H_4Fe(CN)_6,$$

golden needles, decomp. 330°. The action of bromine on 1-*m*-nitro-3-antipyrine in glacial acetic acid solution, leads to the formation of 4-*bromo*-1-m-*nitro*-3-*antipyrine*,  $CMe<\begin{matrix}N(C_6H_4\cdot NO_2)\cdot NMe \\ CBr{-\!-\!-\!-}C\end{matrix}>O$, which separates from alcohol in yellow crystals, m. p. 200°.

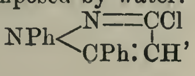
1 : 4-*Dinitro*-3-*antipyrine*,  $CMe<\begin{matrix}N(C_6H_4\cdot NO_2)\cdot NMe \\ C(NO)_2{-\!-\!-\!-}C\end{matrix}>O$, prepared by treating the nitropyrine with cooled concentrated nitric acid, separates from dilute acetic acid in yellow crystals, m. p. 271° (explodes).

1-m-*Amino*-3-*antipyrine*, $NH_2\cdot C_6H_4\cdot C_3N_2OHMe_2$, prepared by reduction of nitro-3-antipyrine with tin and hydrochloric acid, separates from dilute alcohol in white crystals, m. p. 155°. The *acetyl* derivative, $NHAc\cdot C_6H_4\cdot C_3N_2OHMe_2,2H_2O$, m. p. 112°, or, when anhydrous, 199°.

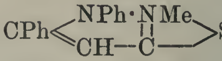
1 : 4-*Diamino*-3-*antipyrine*, $NH_2\cdot C_6H_4\cdot C_3N_2OMe_2\cdot NH_2$, prepared by reduction of dinitro-3-antipyrine with tin and alcoholic hydrogen chloride, forms white crystals, m. p. 185°.

1-m-*Nitro*-3-*thiopyrine*,  $CMe<\begin{matrix}N(C_6H_4\cdot NO_2)\cdot NMe \\ CH{-\!-\!-\!-}C\end{matrix}>S$, formed together with 1-m-*amino*-3-*antipyrine* by the action of potassium hydrogen sulphide on 3-chloro-1-*m*-nitrophenyl-5-methylpyrazole, is obtained as a yellow, microcrystalline powder, m. p. 242·5°, and is only sparingly soluble in hot water. The amino-compound forms white crystals, m. p. 97°, is readily soluble in hot water, and gives an intense yellow coloration with sulphurous acid.

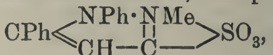
2. 1 : 5-*Diphenyl*-3-*pyrazolone and its Derivatives*.—[With WALTER WILLERT.]—The *sodium* salt of 1 : 5-diphenyl-3-pyrazolone, $C_{15}H_{11}ON_2Na$, crystallises in needles, and is decomposed by water.

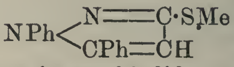
3-*Chloro*-1 : 5-*diphenylpyrazole*,  $NPh<\begin{matrix}N{=\!=}CCl \\ CPh\colon CH\end{matrix}$, crystallises in

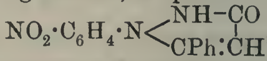
colourless needles, m. p. 64°. The *methiodide*, $C_{15}H_{11}N_2Cl,MeI$, prepared by way of the methosulphate, forms white crystals, m. p. 138°. The *methochloride* ("1 : 5-*diphenylantipyrine chloride*"), $C_{15}H_{11}N_2Cl,MeCl$, prepared by the action of silver chloride on the methiodide, or by heating diphenylantipyrine with phosphoryl chloride at 80°, is obtained as a white, hygroscopic powder, m. p. about 145°, decomp. 40° when moist; the *platinichloride*, $(C_{15}H_{11}N_2Cl,MeCl)_2PtCl_4$, crystallises in red needles, m. p. 288°.

1 : 5-*Diphenyl*-2-*methyl*-3-*thiopyrazolone*,  $CPh\Big<\begin{array}{l}NPh\cdot NMe\\ CH{-}{-}C\end{array}\Big>S$, formed by the action of potassium hydrogen sulphide on the methiodide or the methosulphate, or on the product obtained by heating "diphenylantipyrine" with phosphoryl chloride, separates in strongly refracting, yellow crystals, m. p. 185°; the *platinichloride*,

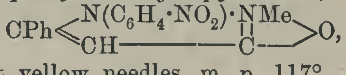
$$(C_{16}H_{14}N_2S)_2,H_2PtCl_6,$$

forms a reddish-yellow, microcrystalline powder; the *methiodide*, $C_{16}H_{14}N_2S,MeI$, crystallises in colourless needles, m. p. 213°; the *ethiodide*, m. p. 188°; the *trioxide*,  $CPh\Big<\begin{array}{l}NPh\cdot NMe\\ CH{-}{-}C\end{array}\Big>SO_3$, crystallises in white needles, m. p. above 300°.

3-*Thiomethyl*-1 : 5-*diphenylpyrazole*,  $NPh\Big<\begin{array}{l}N{=}{=}C\cdot SMe\\ CPh{=}CH\end{array}$, formed on distillation of "diphenylthiopyrine" or its methiodide, crystallises in yellow tablets, m. p. 62°. The 4-*nitroso*-derivative, $SMe\cdot C_3N_2Ph_2\cdot NO$, crystallises in green leaflets, m. p. 145° (decomp.). The *sulphone*, $C_3N_2HPh_2\cdot SO_2Me$, crystallises in glistening needles, m. p. 121°.

5-*Phenyl*-1-m-*nitrophenyl*-3-*pyrazolone*,  $NO_2\cdot C_6H_4\cdot N\Big<\begin{array}{l}NH{-}CO\\ CPh{:}CH\end{array}$, prepared by condensation of acetyl-*m*-nitrophenylhydrazide with ethyl benzoylacetoacetate in presence of phosphorus trichloride, crystallises in light yellow needles, m. p. 264°, and does not yield a nitroso- or an azo-derivative. The *sodium* salt, $C_{15}H_{10}O_3N_3Na$, forms orange-yellow needles, and detonates and inflames when heated.

5-*Phenyl*-1-m-*nitrophenyl*-2-*methyl*-3-*pyrazolone*,

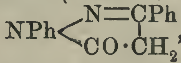


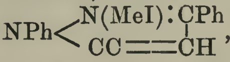
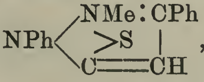
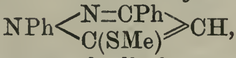
$$CPh\Big<\begin{array}{l}N(C_6H_4\cdot NO_2)\cdot NMe\\ CH{-}{-}{-}{-}C\end{array}\Big>O,$$

crystallises in light yellow needles, m. p. 117°. The corresponding 3-*chloropyrazole*, $C_{15}H_{10}N_2Cl\cdot NO_2$, forms light yellow needles, m. p. 115°; the *methiodide*, $C_{15}H_{10}N_2Cl\cdot NO_2,MeI$, crystallises in yellow needles, m. p. 169°.

5-*Phenyl*-1-m-*nitrophenyl*-2-*methyl*-3-*thiopyrazolone*, $C_{16}H_{13}N_2S\cdot NO_2$, is obtained as a yellow, microcrystalline powder, m. p. 112°; the *platinichloride*, $(C_{16}H_{13}N_2S\cdot NO_2)_2,H_2PtCl_6$, orange-red powder; the *methiodide*, $NO_2\cdot C_{16}H_{13}N_2S,MeI$, crystallises in yellow needles, m. p. 172° (decomp.); the *trioxide*, $C_{16}H_{13}O_5N_3S$, crystallises in yellow needles, decomp. 285°. The action of nitric acid on diphenyl-3-thiopyrine in concentrated sulphuric acid solution leads to the formation of a *trioxide*, $C_{16}H_{12}O_3N_2S(NO_2)_2$, which is obtained as a yellow powder.

G. Y.

1 : 3-Diphenyl-5-pyrazolone and its 1-Nitro-derivative. AUGUST MICHAELIS and WALTER WILLERT (*Annalen*, 1907, **358**, 171—182).—1 : 3-Diphenyl-5-pyrazolone,  $\mathrm{NPh}<\begin{matrix}\mathrm{N{=}CPh}\\ \mathrm{CO\cdot CH_2}\end{matrix}$, and some of its derivatives were prepared by Knorr and Klotz (Abstr., 1887, 1121). The present paper contains an account of a number of other derivatives which have not been described previously.

5-*Chloro*-1 : 3-*diphenylpyrazole*, $C_3N_2HClPh_2$, prepared by heating diphenyl-5-pyrazolone with phosphoryl chloride at 150—160°, or together with methyl chloride by heating diphenyl-5-antipyrine with phosphoryl chloride, forms colourless crystals, m. p. 49°. The *methiodide*,  $\mathrm{NPh}<\begin{matrix}\mathrm{N(MeI){:}CPh}\\ \mathrm{CC{=}CH}\end{matrix}$, formed by conversion of chlorodiphenylpyrazole into its *methosulphate* and treatment of this with potassium iodide, crystallises in white needles, m. p. 172°. The *methochloride* ("1 : 3-*diphenylantipyrine chloride*") forms white crystals, m. p. 194°, and is less hygroscopic than the corresponding 1 : 5-diphenyl derivative. The *platinichloride*, $(C_{15}H_{11}N_2Cl)_2PtCl_4$, crystallises in orange-red needles, m. p. 222°. The action of potassium hydrogen sulphide on the methiodide leads to the formation of 1 : 3-*diphenyl*-2-*methyl*-5-*thiopyrazolone*,  $\mathrm{NPh}<\begin{matrix}\mathrm{NMe{:}CPh}\\ {>}\mathrm{S}\\ \mathrm{C{=}CH}\end{matrix}$, which crystallises from alcohol in yellow needles, m. p. 163°, and gives with ferric chloride a transient brown coloration, or an intense yellow coloration with sulphurous acid. The *platinichloride*, $(C_{16}H_{14}N_2S)_2,H_2PtCl_6$, forms a crystalline powder, decomp. when heated; the *methiodide*, $C_{16}H_{14}N_2S,MeI$, crystallises in white needles, m. p. 185°; the *ethiodide*, white needles, m. p. 167°; the *trioxide*, $C_{16}H_{14}N_2SO_3$, nacreous leaflets, decomp. above 300°. 5-*Thiomethyl*-1 : 3-*diphenylpyrazole* ("*diphenyl*-5-*ψ*-*thiopyrine*"),  $\mathrm{NPh}<\begin{matrix}\mathrm{N{=}CPh}\\ \mathrm{C(SMe)}\end{matrix}>\mathrm{CH}$, is obtained as a colourless oil, b. p. 225°/11 mm., gradually becomes yellow, and does not form a nitroso-derivative. The *hydrochloride*, $C_{16}H_{14}N_2S,HCl,2H_2O$, crystallises in needles, m. p. 80°, and is decomposed by water. The *sulphone*, $C_{16}H_{14}N_2SO_2$, crystallises in silky needles, m. p. 162°.

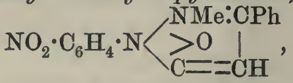
4-*Benzeneazo*-5-*chloro*-1 : 3-*diphenylpyrazole*, $N_2Ph\cdot C_3N_2ClPh_2$, prepared by heating 4-benzeneazo-1 : 3-diphenyl-5-pyrazolone with phosphoryl chloride at 110—115°, crystallises from alcohol in orange-red needles, m. p. 122°, is insoluble in alkalis, and on reduction with zinc dust and alcoholic potassium hydroxide yields 4-*benzeneazo*-1 : 3-*diphenylpyrazole*, $N_2Ph\cdot C_3N_2Ph_2$, which crystallises in orange-red needles, m. p. 111°, and gives an intense red coloration when heated with concentrated hydrochloric acid; the *hydrochloride*, $C_{21}H_{16}N_4,HCl$, crystallises in red needles, decomp. about 100°.

3-*Phenyl*-1-m-*nitrophenyl*-5-*pyrazolone*, $C_3HON_2Ph\cdot C_6H_4\cdot NO_2$, prepared from ethyl benzoylacetate and *m*-nitrophenylhydrazine, forms light yellow needles, m. p. 174°. The 4-*benzeneazo*-derivative,

$$N_2Ph\cdot C_3HON_2Ph\cdot C_6H_4\cdot NO_2,$$

prepared by the action of diazobenzene chloride on the pyrazolone in aqueous sodium hydroxide solution and acidification of the mixture with acetic acid, crystallises from alcohol in orange-red needles, m. p. 179°, and is soluble in aqueous alkalis. The corresponding 4-*benzeneazo-5-chloro*-compound, $C_{15}H_9N_2Cl(NO_2)\cdot N_2Ph$, forms reddish-brown crystals, m. p. 152°.

3-*Phenyl*-1-m-*nitrophenyl*-2-*methyl*-5-*pyrazolone*,



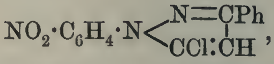
$$NO_2\cdot C_6H_4\cdot N\left<\begin{matrix} NMe{:}CPh \\ >O \quad | \\ C{=}{=}CH \end{matrix}\right. ,$$

prepared by heating nitrodiphenylpyrazolone with methyl sulphate and liberating the base with a dilute alkali, crystallises from alcohol in light yellow needles, m. p. 178°, and resembles antipyrine in its behaviour towards ferric chloride and nitrous acid, but is much less basic than that substance. The *platinichloride*,

$$(C_{16}H_{13}O_3N_3)_2,H_2PtCl_6,$$

forms orange-red needles, m. p. 230°; the *hydriodide*, $C_{16}H_{13}O_3N_3,HI$, crystallises from alcohol in yellow needles; the *nitroso*-derivative, $C_{16}H_{12}O_3N_3\cdot NO$, crystallises in green leaflets, darkens at 215°, m. p. 225° (decomp.).

5-*Chloro-3-phenyl*-1-m-*nitrophenylpyrazole*,



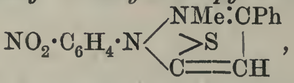
$$NO_2\cdot C_6H_4\cdot N\left<\begin{matrix} N{=}CPh \\ CCl{:}CH \end{matrix}\right. ,$$

prepared in the same manner as 5-chlorodiphenylpyrazole, crystallises in slightly yellow needles, m. p. 105°; the *methiodide*,

$$C_{15}H_{10}O_2N_3Cl,MeI,$$

formed by way of the methosulphate, crystallises in dark yellow needles, m. p. 172°.

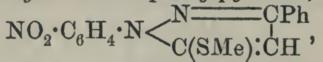
3-*Phenyl*-1-m-*nitrophenyl*-2-*methyl*-5-*thiopyrazolone*,



$$NO_2\cdot C_6H_4\cdot N\left<\begin{matrix} NMe{:}CPh \\ >S \quad | \\ C{=}{=}CH \end{matrix}\right. ,$$

prepared by the action of potassium hydrogen sulphide on the methiodide, is obtained as a yellowish-brown powder, m. p. 158°; the *platinichloride*, $(NO_2\cdot C_{16}H_{13}N_2S)_2,H_2PtCl_6$, orange-red powder, decomp. when heated; the *methiodide*, $C_{16}H_{13}N_2S(NO_2)MeI$, yellow needles, m. p. 202°; the *trioxide*, $NO_2\cdot C_{16}H_{13}N_2SO_3$, yellow crystals, m. p. 300°.

5-*Thiomethyl-3-phenyl*-1-m-*nitrophenylpyrazole*,



$$NO_2\cdot C_6H_4\cdot N\left<\begin{matrix} N{=}{=}{=}CPh \\ C(SMe){:}CH \end{matrix}\right. ,$$

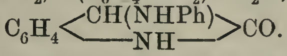
prepared by heating the methiodide in a vacuum, crystallises from alcohol in yellow needles, m. p. 106°; the *sulphone*, $NO_2\cdot C_{16}H_{13}N_2SO_2$, forms white needles, m. p. 148°. G. Y.

Action of Dichloroacetic Acid on Aniline and its Homologues. II. Gustav Heller (*Annalen*, 1908, **358**, 349—373. Compare Abstr., 1904, i, 730).—In amplification of the previous paper, further details are given as to the nitration of stilbenedicarboxylic acid, the preparation of 3:3′-dinitrostilbenedicarboxylic acid is described, and the action of dichloroacetic acid on aniline and its homologues is discussed in the light of results obtained with *m*-toluidine and the xylidines. The first product of the action of dichloroacetic acid on aniline or a homologue is a substance of the type (*a*) $CH(NHPh)_2\cdot CO_2H$, (*b*) $NHPh\cdot CHCl\cdot CO_2H$, or (*c*) $NHPh\cdot CHCl\cdot CO\cdot NHPh$. These are not isolated, but immediately undergo isomerisation alone, or followed by condensation, (*a*) yielding a product of the type (I)

$$NH_2\cdot C_6H_4\cdot CH(NHPh)\cdot CO_2H$$

or (II) $CH(C_6H_4\cdot NH_2)_2\cdot CO_2H$, (*b*) a product of the type (III)

$$CO_2H\cdot C(C_6H_4\cdot NH_2)\colon C(C_6H_4\cdot NH_2)\cdot CO_2H,$$

and (*c*) a product of type (IV)  $C_6H_4\Big<\substack{CH(NHPh)\\NH}\Big>CO$. Products of type (I) are obtained in the case of *o*-toluidine and *v*-*m*-xylidine, (II) is obtained from *p*-xylidine, (III) from aniline, *m*-toluidine, and *v*-*o*-xylidine, whilst products of type (IV) are formed from *p*-toluidine, *as*-*m*-xylidine, *s*-xylidine, and 1 : 2 : 4-xylidine.

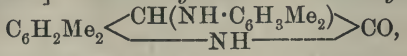
The action of nitric acid, D 1·52, on stilbenedicarboxylic anhydride at 0° and, finally at the ordinary temperature, leads to the formation of a mixture of crystalline acids, which on oxidation with permanganate in dilute sodium hydroxide yield *p*-nitrobenzoic acid together with small amounts of *o*- and probably of *m*-nitrobenzoic acids. Reduction of the mixed nitrostilbenedicarboxylic acids leads to the formation of an *acid*, crystallising in needles, decomp. about 180°, and 4 : 4′-diaminostilbenedicarboxylic acid, together with traces of nitro- or azoxy-compounds.

m-Nitrobenzyl cyanide (Gabriel, Abstr., 1883, 916), formed together with a *substance*, m. p. 149°, insoluble in hot ether, from the chloride and potassium cyanide in aqueous solution at 50—60°, separates from a mixture of ether and light petroleum in crystals, m. p. 61—62°. On successive treatment with iodine and sodium methoxide in methyl alcohol-ethereal solution, *m*-nitrobenzyl cyanide yields 3 : 3′-*dinitrodicyanostilbene*, $C_{16}H_8O_4N_4$, which crystallises in colourless plates or short prisms, m. p. 233° (decomp.); on reduction with stannous chloride and hydrogen chloride in acetic acid solution, it is converted into the 3 : 3′-*diamino*-compound, $C_{16}H_{12}N_4$, crystallising in threads, m. p. 187°, and forming a sparingly soluble, colourless *hydrochloride*. 3 : 3′-*Dinitrostilbenedicarboxylic anhydride*, $C_{16}H_8O_7N_2$, prepared by heating the dicyanide with hydrogen chloride in glacial acetic acid solution at 185—190°, forms colourless needles, m. p. 249—249·5°. The dinitro-anhydride could not be reduced in acid solution; with zinc dust and ammonia in sodium hydroxide solution, it yields 3 : 3′-*azoxystilbenedicarboxylic anhydride*, $C_{16}H_8O_4N_2$, obtained as a yellow powder, decomp. slowly above 245°. 3 : 3′-*Diaminostilbenedicarboxylic anhydride*, $C_{16}H_8O_4N_2$, formed from the dicyanide by hydrolysis with alcoholic alkali, is obtained in red, amorphous masses, soluble in ethyl benzoate.

2 : 2′-*Azoxystilbenedicarboxylic anhydride*, prepared by reduction of the 2 : 2′-dinitro-acid with stannous chloride and hydrochloric acid or with boiling zinc dust and ammonia, remains unchanged at 270°, and dissolves in dilute sodium carbonate, forming the yellow sodium salt of the dicarboxylic acid. The reduction appears to proceed further if the dinitro-acid is treated with stannous chloride in glacial acetic acid solution.

The action of sodium dichloroacetate on *m*-toluidine in sodium acetate solution leads to the formation of a crystalline *hydrochloride*, decomposing when highly heated; the free *amino*-compound behaves in the same manner as the acids derived from dichloroacetic acid and aniline, or *o*- or *p*-toluidines.

[With P. LEYDEN.]—3-as-m-*Xylidino*-5 : 7-*dimethyloxindole*,



$$\mathrm{C_6H_2Me_2}<\begin{matrix}\mathrm{CH(NH\cdot C_6H_3Me_2)}\\ \mathrm{NH}\end{matrix}>\mathrm{CO},$$

prepared from dichloroacetic acid and 1 : 3 : 4-xylidine, crystallises in needles, m. p. about 234°, forms a *bromo*-derivative, $C_{18}H_{19}ON_2Br$, m. p. about 215°, and, when treated with bromine in hot glacial acetic acid solution, is oxidised to 5 : 7-*dimethylisatin*, $C_{10}H_9O_2N$, crystallising in yellow needles, m. p. 243°. The *phenylhydrazone* of this, $C_{16}H_{15}ON_3$, yellow needles, m. p. 272°.

3′ : 5′-*Xylidino*-4 : 6-*dimethyloxindole*, prepared from dichloroacetic acid and 1 : 3 : 5-xylidine, crystallises in needles, m. p. 250° (decomp.). 4 : 6-*Dimethylisatin*, yellow needles, m. p. 238—239°; the *phenylhydrazone*, yellow needles, m. p. 238—239°.

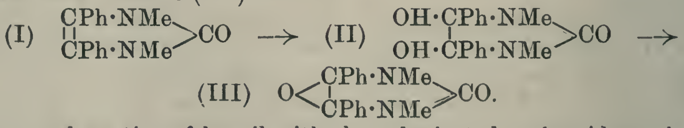
Di-4-*amino*-2 : 5-*dimethylphenylacetic acid*,

$$\mathrm{CH(C_6H_2Me_2\cdot NH_2)_2\cdot CO_2H},$$

formed from dichloroacetic acid and *p*-xylidine, is obtained in granular crystals, m. p. 245° (decomp.); the *hydrochloride*, $C_{18}H_{22}O_2N_2,2HCl$, needles; the *sulphate* is only very sparingly soluble. The *dibenzoyl* derivative, $C_{32}H_{30}O_4N_2$, needles, m. p. 182—183°. When diazotised and coupled with β-naphthol, the base forms the *bisazonaphthol*, $CH(C_6H_2Me_2\cdot N_2\cdot C_{10}H_6\cdot OH)_2\cdot CO_2H$, which crystallises in red needles, softens at 195°, and gradually decomposes at the higher temperature.

Ostromisslensky's paper on the same subject (this vol., i, 82) is criticised. G. Y.

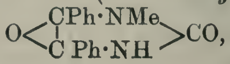
Action of Methylcarbamides on Benzil. HEINRICH BILTZ [with P. HORRMANN and RIMPEL] (*Ber.*, 1908, 41, 167—173).—An investigation of the compounds formed by the condensation of methylcarbamide and *s*-dimethylcarbamide with benzil. Unlike glyoxal and diacetyl (Biltz and Horrmann, this vol., i, 62), benzil condenses with only 1 mol. of methylcarbamide or *s*-dimethylcarbamide. The products so formed may also be prepared from glyoxalones; for example, 4 : 5-diphenyl-1 : 3-dimethylglyoxalone (I), when oxidised by potassium permanganate in aqueous acetone, is converted into 4 : 5-dihydroxy-4 : 5-diphenyl-1 : 3-dimethylglyoxalone (II), which compound readily loses water when heated at 180° or boiled with acetic anhydride, being converted into a substance identical with that formed by the condensation of *s*-dimethylcarbamide with benzil, and which, from its mode of formation from the glyoxalone, must be 4 : 5-diphenyl-1 : 3-dimethylglyoxalone-4 : 5-oxide (III):



$$\text{(I)}\ \begin{matrix}\mathrm{CPh\cdot NMe}\\ \|\\ \mathrm{CPh\cdot NMe}\end{matrix}>\mathrm{CO}\ \longrightarrow\ \text{(II)}\ \begin{matrix}\mathrm{OH\cdot CPh\cdot NMe}\\ |\\ \mathrm{OH\cdot CPh\cdot NMe}\end{matrix}>\mathrm{CO}\ \longrightarrow$$

$$\text{(III)}\ \mathrm{O}<\begin{matrix}\mathrm{CPh\cdot NMe}\\ |\\ \mathrm{CPh\cdot NMe}\end{matrix}>\mathrm{CO}.$$

The condensation of benzil with the substituted carbamide probably takes place in two stages, the compound first formed being the glycol, which then decomposes with the elimination of water.

4 : 5-*Diphenyl*-1-*methylglyoxalone*-4 : 5-*oxide* (4 : 5-*endoxy*-2-*oxy*-4 : 5-*diphenyl*-1-*methyltetrahydroglyoxaline*,  $\mathrm{O}<\begin{matrix}\mathrm{CPh\cdot NMe}\\ |\\ \mathrm{CPh\cdot NH}\end{matrix}>\mathrm{CO}$, results on

heating benzil with methyl carbamide at 145°; it crystallises in rhombic leaflets, m. p. 216—217°; the *acetate*, $C_{18}H_{16}O_3N_2$, crystallises in small rhombohedra, m. p. 172°.

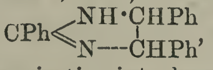
4 : 5-*Dihydroxy*-4 : 5-*diphenyl*-1 : 3-*dimethylglyoxalone*, $C_{17}H_{18}O_3N_2$, prepared by the oxidation of 4 : 5-diphenyl-1 : 3-dimethylglyoxalone (Biltz and Horrmann, this vol., i, 57), crystallises in long, flat, rectangular plates, m. p. 205° (decomp.). When heated with acetic anhydride or alone at 180°, it loses water, yielding 4 : 5-*diphenyl*-1 : 3-*dimethylglyoxalone*-4 : 5-*oxide* (4 : 5-*endoxy*-2-*oxy*-4 : 5-*diphenyl*-1 : 3-*dimethyltetrahydroglyoxaline*), $C_{17}H_{16}O_2N_2$, crystallising in flat, six-sided plates, m. p. 197—198°; the same compound is obtained on heating benzil with *s*-dimethylcarbamide at 205°.

Benzil behaves like benzoin when heated with *as*-dimethylcarbamide, diphenylacetylenediureine being formed (compare Anschütz and Geldermann, Abstr., 1891, 725).

Attempts to prepare 4 : 5-diphenylglyoxalone-4 : 5-oxide were unsuccessful. W. H. G.

Interaction of Sodium Sulphide and the Hydroxyphenazines. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 187868).—The hydroxyphenazines derived from the meta-diamines and the chlorinated *p*-aminophenols, containing one or two chlorine atoms in the ortho-positions with respect to the hydroxyl group when heated with crystallised sodium sulphide at 110—140°, give rise to sulphur derivatives which no longer contain chlorine. These sulphur compounds are reddish-brown powders, sparingly soluble in water, alcohol, or dilute acids; they dye cotton only very slightly, and seem to be intermediate products in the formation of sulphide dyes, as they are converted into these substances by further treatment with sodium sulphide and sulphur. The properties of a series of these intermediate sulphur derivatives are tabulated in the patent. G. T. M.

Resolution of the Iminazole Ring in the Case of Amarine and Anisine. Otto Fischer and Georg Prause (*J. pr. Chem.*, 1908, [ii], 77, 125—134).—The resolution of the iminazole ring of amarine and anisine has been studied in extension of the investigations on this subject already published (Abstr., 1906, i, 539; 1907, i, 352).

Amarine, $C_{21}H_{18}N_2,\frac{1}{2}H_2O$ (Bertagnini, *Annalen*, 1853, 88, 127), crystallises from dilute alcohol in pointed rhombohedra, m. p. 106°, loses $\frac{1}{2}H_2O$ at 100—110° or when boiled with water (Claus, Abstr., 1885, 1063), and when anhydrous crystallises from benzene-light petroleum in colourless prisms, m. p. 133°. The formation of dibenzylidenediaminostilbene on reduction of amarine with sodium (Grossmann, Abstr., 1889, 1191) is considered to take place in several stages, the amarine,  $\mathrm{CPh}{<}\begin{array}{l}\mathrm{NH{\cdot}CHPh}\\ \qquad\vert\\ \mathrm{N{-}{-}{-}CHPh}\end{array}$, being reduced to hydroamarine, which undergoes isomerisation into benzylidenediaminostilbene,

$$NH_2{\cdot}CHPh{\cdot}CHPh{\cdot}N{:}CHPh,$$

and hydrobenzamide, which is further reduced to benzylideneimine, $CHPh{:}NH$, and this reacts with the monobenzylidene compound forming ammonia and dibenzylidenediaminostilbene,

$$CHPh\colon N\cdot CHPh\cdot CHPh\cdot N\colon CHPh.$$

In agreement with this view, it is found that ammonia is evolved during the reduction, and that the yield of the dibenzylidene compound is increased by addition of hydrobenzamide to the reaction mixture.

cis-*Diaminostilbene picrate*, $C_{26}H_{22}O_{14}N_8$, has m. p. 239°. The *diformyl* derivative, $C_{16}H_{16}O_2N_2$, crystallises in colourless prisms, m. p. 294°.

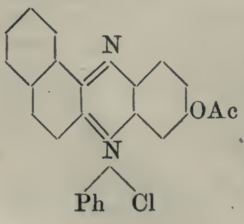
*iso*Amarine is obtained in an almost quantitative yield by heating amarine with sodium ethoxide in alcoholic solution at 150—160°.

p-Anisine crystallises from dilute alcohol in needles (H_2O), m. p. 118°, or when anhydrous from benzene-light petroleum in prisms, m. p. 148°. On reduction with sodium, it forms ammonia and *dianisylidenedi*-p-*methoxydiaminostilbene*, $C_{32}H_{32}O_4N_2$, which crystallises in colourless leaflets, m. p. 183°, and when heated with dilute acids yields anisaldehyde and *di*-p-*methoxydiaminostilbene*, $C_{16}H_{20}O_2N_2$, crystallising in needles, m. p. 151°; the *hydrochloride*, $C_{16}H_{20}O_2N_2,2HCl$, needles, decomp. about 260°; the *picrate* (H_2O), yellow prisms, m. p. about 215° (decomp.). The *diformyl* derivative, $C_{18}H_{20}O_4N_2$, crystallises in leaflets, m. p. 290° (decomp.); the *diacetyl* derivative, $C_{20}H_{24}O_4N_2$, prisms, m. p. about 330° (decomp.). The action of nitrous acid on the diamine leads to the formation of the *amino-alcohol*,

$$OMe\cdot C_6H_4\cdot CH(NH_2)\cdot CH(OH)\cdot C_6H_4\cdot OMe,$$

which crystallises from light petroleum in colourless prisms, m. p. 134°. The diamine condenses with anisaldehyde to form dianisylidenedimethoxydiaminostilbene, m. p. 183°, or with benzaldehyde, yielding *dibenzylidenedimethoxydiaminostilbene*, $C_{30}H_{28}O_2N_2$, which crystallises in colourless prisms, m. p. 148°, and is hydrolysed by boiling dilute sulphuric acid, forming benzaldehyde and the diamine. G. Y.

Constitution of Rosindone and *iso*Rosindone. Friedrich Kehrmann and K. L. Stern (*Ber.*, 1908, **41**, 12—17).—The phenolbetaine formula for *iso*rosindone, which has been supported by Decker and Würsch on negative grounds (Abstr., 1906, i, 905), is confirmed by a study of its behaviour towards acetic anhydride and zinc dust. *Leuco*-iso*rosindone diacetate*, $C_{10}H_6<\substack{NAc\\NPh}>C_6H_3\cdot OAc$, prepared in this way, crystallises from alcohol in small, colourless, glistening plates, m. p. 215° (decomp.). Ferric chloride oxidises it, yielding the ferrichloride of 3-*acetoxyphenylnaphthaphenazonium chloride*, annexed formula, which forms yellowish-brown crystals, decomposing slowly in aqueous solution into *iso*rosindone. When *iso*rosindone is kept in contact with acetic anhydride for two months at the ordinary temperature, and afterwards ferric chloride added to its aqueous solution, the same double salt is formed, a reaction quite analogous to that of naphthaprasindone (Abstr., 1899, i, 528). The conclusion is drawn that addition



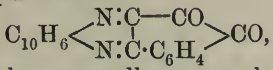
of acetic anhydride occurs, forming the phenazonium acetate, this being converted into chloride by the ferric chloride.

Leuco-2-methylisorosindone diacetate forms plates, m. p. 242°, and, on oxidation with ferric chloride, yields the ferrichloride of 2-*methyl*-3-*acetoxyphenylnaphthaphenazonium chloride*, $C_{25}H_{19}O_2N_2Cl,FeCl_3$. The *chloride* itself is red; its *platinichloride*, $(C_{25}H_{19}O_2N_2)_2PtCl_6$, fiery-red, and the *nitrate*, brick-red.

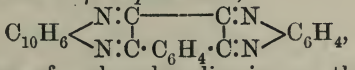
An alcoholic solution of 2-methyl*iso*rosindone, when treated with ferric chloride, gives a metallic green double salt, which, in contradistinction to the corresponding acetoxy-compound, is insoluble in water.

Leuco-rosindone diacetate is not well characterised; on oxidation with ferric chloride, it gives the ferrichloride of 6-*acetoxyphenylnaphthaphenazonium chloride*, $C_{24}H_{17}O_2N_2Cl,FeCl_3$, slowly passing back in water to rosindone. W. R.

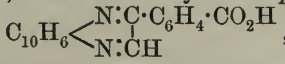
Oxidation of Naphthazines by Chromic Acid. III. Relation of the Azines to the Quinoxalines. OTTO FISCHER and ERICH SCHINDLER (*Ber.*, 1908, **41**, 390—397. Compare Abstr., 1904, i, 111; 1906, i, 609).—The method of preparing diketonaphthaphenazine by oxidising naphthaphenazine with chromic acid has now been applied to the oxidation of the naphthazines. Progressive degradation to quinoxaline bases has been accomplished in the case of both the naphthazines and naphthaphenazine. The phenazines, quinoxalines, and pyrazines (Gabriel and Sonn, this vol., i, 60) are thus shown to be members of the same group of azines.

Diketo-s-*aβ-naphthazine*,  $C_{10}H_6<\begin{matrix}N:C—CO\\ N:C\cdot C_6H_4\end{matrix}>CO$, crystallises from boiling anisole in yellowish-brown needles, m. p. about 300° (decomp.). In the absence of acetic anhydride, the oxidation leads to the formation of mixed crystals of the diketo-product and unchanged *s-aβ*-naphthazine. The diketone is reduced by phenylhydrazine in hot glacial acetic acid solution, forming the *dihydroxynaphthazine*, crystallising in brown needles, and gives with alcoholic potassium hydroxide a blue, or with concentrated sulphuric acid a green, coloration. The *diacetyl* derivative, $C_{24}H_{16}O_4N_2$, crystallises in yellow needles, m. p. above 270° (decomp.). The *monoxime*, $C_{20}H_{11}O_2N_3$, crystallises from pyridine in needles, and gives a brown coloration with concentrated sulphuric acid.

aβ-Naphthaphenazine-s-*aβ-naphthazine*,



$$C_{10}H_6<\begin{matrix}N:C——C:N\\ N:C\cdot C_6H_4\cdot C:N\end{matrix}>C_6H_4,$$

formed by the action of *o*-phenylenediamine on the diketone at 130°, crystallises in yellow needles, and with mineral acids yields red *salts*, which are hydrolysed by water. When boiled with concentrated sodium hydroxide, the diketone yields 2-*phenylnaphthaquinoxaline*-o-*carboxylic acid*,  $C_{10}H_6<\begin{matrix}N:C\cdot C_6H_4\cdot CO_2H\\ N:CH\end{matrix}$, crystallising in yellow needles, m. p. above 300° (decomp.), sublimes partially unchanged, and gives a cherry-red coloration with sulphuric acid. When distilled, it loses carbon dioxide and forms 2-*phenylnaphthaquinoxaline*, $C_{18}H_{12}N_2$, which crystallises in yellow needles, m. p. 153°, sublimes unchanged, and gives a dark red coloration with sulphuric acid.

as-$\alpha\beta$-Naphthazine give a similar series of derivatives.

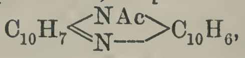
Diketo-as-*$\alpha\beta$-naphthazine*, $C_{20}H_{10}O_2N_2$, crystallises in red needles, commences to darken at 240°, cokes when highly heated, and is reduced easily by phenylhydrazine in glacial acetic acid-acetic anhydride solution, yielding a blue *product*, which on exposure to air in presence of alcohol or acetic acid again forms the diketone. The *monoxime* crystallises in yellow needles.

$\alpha\beta$-Naphthaphenazine-as-*$\alpha\beta$-naphthazine*, $C_{20}H_{14}N_4$, forms yellow needles, m. p. about 284°, and yields dark red *salts* with concentrated mineral acids. 3-*Phenylnaphthaquinoxaline*-o-*carboxylic acid* sublimes in long needles, m. p. 246° (decomp.). 3-*Phenylnaphthaquinoxaline* crystallises in yellow needles, m. p. 163°.

Whilst oxidation of the alkylhydroxides of phenazine and naphthaphenazine in alkaline solution leads to the formation of *N*-alkyl*apo*-safranone and rosindone respectively, the quinoxalines under these conditions behave in the same manner as quinolines, yielding quinoxalones. Thus N-*methylnaphthaquinoxalone*, $C_{13}H_{10}ON_2$, which crystallises in yellow prisms, m. p. 214°, is obtained by oxidising $\alpha\beta$-naphthaquinoxaline methiodide, $C_{13}H_{11}N_2I$, red prisms, decomp. above 150°, with alkaline ferricyanide solution. G. Y.

$\alpha\beta$-Naphthazines. Otto Fischer and Heinrich Straus (*Ber.*, 1908, **41**, 397—400).—A method of preparing unstable azo-dyes, and a note on the simultaneous formation of α- and β-naphthazines. Azo-dyes, such as benzeneazo-$\beta\beta$-dinaphthylamine (Matthes, Abstr., 1890, 992), which are readily decomposed by acids, and diazoamino-compounds, which easily undergo isomerisation into aminoazo-compounds, are obtained with ease in a state of purity if prepared in pyridine solution. The following azo-dyes have been prepared in this manner from $\beta\beta$-dinaphthylamine.

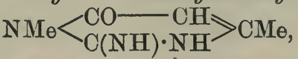
p-*Chlorobenzene-$\beta\beta$-dinaphthylamine*, $C_{26}H_{18}N_3Cl$, violet-red needles, m. p. 165°. p-*Tolueneazo-$\beta\beta$-dinaphthylamine*, $C_{27}H_{21}N_3$, scarlet needles, m. p. 172°. m-*Xyleneazo-$\beta\beta$-dinaphthylamine*, from 4-amino-*m*-xylene, red prisms, m. p. 130°. *α-Naphthaleneazo-$\beta\beta$-dinaphthylamine*, $C_{30}H_{21}N_3$, a red, crystalline mass, m. p. 204°. *β-Naphthaleneazo-$\beta\beta$-dinaphthylamine*, dark violet needles, m. p. 205°. When treated with glacial acetic acid and heated with hydrochloric acid on the water-bath, these azo-dyes are converted into $\alpha\beta$-naphthazine, m. p. 243°.

Acetyldihydro-s-*$\alpha\beta$-naphthazine*,  $C_{10}H_7{<}\genfrac{}{}{0pt}{}{NAc}{N\text{---}}{>}C_{10}H_6$, formed by boiling the naphthazine with acetic anhydride and glacial acetic solution, crystallises in yellow prisms, m. p. 228°.

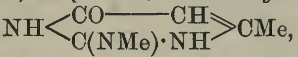
The action of β-naphthaquinone on $\alpha\beta$-dinaphthylamine (Witt, 1887, 153) leads to the formation, not only of *as*-$\alpha\beta$-naphthazine, but also of the *s*-isomeride, which, in two experiments, was obtained as the chief product. G. Y.

Condensation of Alkylguanidines with Ethyl Acetoacetate, &c. Riko Majima (*Ber.*, 1908, **41**, 176—186).—A continuation of the investigation on the anhydro-bases derived from aliphatic diamines (Haga and Majima, Abstr., 1903, i, 291). Alkylguanidines condense with unsymmetrical compounds, like ethyl acetoacetate, with the formation of two isomeric dialkyl derivatives of 2-imino-4-oxytetrahydropyrimidines, whereas only one compound is formed when the alkylguanidine condenses with a substance having a symmetrical structure such as ethyl malonate or acetylacetone. The constitution of each compound formed was deduced from its behaviour on decomposition with concentrated hydrochloric acid.

Ethyl acetoacetate, when heated with methylguanidine carbonate in alcohol, yields 2-*imino*-6-*oxy*-1 : 4-*dimethyltetrahydropyrimidine*,



$$\mathrm{NMe}<\begin{matrix}\mathrm{CO}\text{——}\mathrm{CH}\\ \mathrm{C(NH)\cdot NH}\end{matrix}>\mathrm{CMe},$$

crystallising in needles, m. p. 312°, and 6-*oxy*-2-*methylimino*-4-*methyltetrahydropyrimidine*,  $\mathrm{NH}<\begin{matrix}\mathrm{CO}\text{——}\mathrm{CH}\\ \mathrm{C(NMe)\cdot NH}\end{matrix}>\mathrm{CMe}$, crystallising in leaflets, m. p. 202°. The former compound was first prepared by Jaeger (Abstr., 1891, 1007) by the methylation of iminomethyluracil, but its constitution was not ascertained; it is converted by concentrated hydrochloric acid under pressure at 170—180° into 1 : 4-dimethyluracil (Behrend and Thurm, Abstr., 1902, i, 832); the *hydrochloride*,

$$C_6H_9ON_3,HCl,H_2O,$$

crystallises in prisms, m. p. 265° (decomp.); the *platinichloride*,

$$(C_6H_9ON_3)_2,H_2PtCl_6,2H_2O,$$

forms orange-red, rhombic crystals, m. p. 207°.

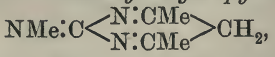
6-Oxy-2-methylimino-4-methyltetrahydropyrimidine is converted by concentrated hydrochloric acid under pressure at 220° into 4-methyluracil; its *hydrochloride*, $C_6H_9ON_3,HCl,\frac{1}{2}H_2O$, m. p. 253°, and *platinichloride*, $(C_6H_9ON_3)_2,H_2PtCl_6$, were prepared.

Allylguanidine sulphate, $(C_4H_9N_3)_2,H_2SO_4$, m. p. 220—222°, results on heating allylamine sulphate and cyanamide in a sealed tube at 110—120°; the *picrate*, $C_4H_9N_3,C_6H_3O_7N_3$, rhombic crystals, m. p. 144—145°, and *platinichloride*, $(C_4H_9N_3)_2,H_2PtCl_6$, m. p. 188° (decomp.), were prepared.

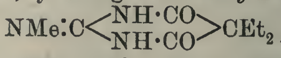
2-*Imino*-6-*oxy*-4-*methyl*-1-*allyltetrahydropyrimidine*, $C_8H_{11}ON_3$, prepared from ethyl acetoacetate and allylguanidine, or by treating iminomethyluracil with allyl iodide in alcohol containing potassium hydroxide, forms crystals, m. p. 182°; the *picrate* has m. p. 205°. When heated with hydrochloric acid under pressure, it yields 4-*methyl*-1-*chloropropyluracil*, $C_8H_{11}O_2N_2Cl$, crystallising in lustrous leaflets, m. p. 208—209°.

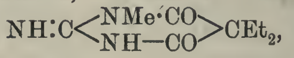
6-*Oxy*-2-*allylimino*-4-*methyltetrahydropyrimidine*, $C_8H_{11}ON_3$, is also formed by the interaction of allylguanidine and ethyl acetoacetate; it has m. p. 149°; the *picrate* forms long prisms, m. p. 182°. It is converted by concentrated hydrochloric acid under pressure at 100° into 2-*chloropropylimino*-4-*methyluracil*, $C_8H_{12}ON_3Cl,H_2O$, crystallising in leaflets, m. p. about 90°, whilst at 150° it is converted into a third isomeride, named provisionally γ-*isomeride*, $C_8H_{11}ON_3$, forming rhombic crystals, m. p. 184—185°; the *picrate* has m. p. 200—201°.

[With KOBAYASKI.]—Acetylacetone and methylguanidine react, yielding 2-*methylimino*-4 : 6-*dimethyldihydropyrimidine*,



$$\mathrm{NMe{:}C}<\begin{matrix}\mathrm{N{:}CMe}\\ \mathrm{N{:}CMe}\end{matrix}>\mathrm{CH_2},$$

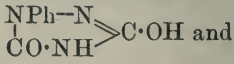
which crystallises in long, glistening prisms, m. p. 98° ; it is converted by hydrochloric acid at 160°, and by nitrous acid at low temperatures, into *acetylacetonecarbamide* (2-*oxy*-4 : 6-*dimethyldihydropyrimidine*). Ethyl diethylmalonate and methylguanidine condense in the presence of sodium ethoxide at 100—110°, yielding 4 : 6-*dioxy*-2-*methylimino*-5 : 5-*diethylhexahydropyrimidine*,  $\mathrm{NMe{:}C}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}>\mathrm{CEt_2}$; it crystallises in rhombic leaflets, m. p. 233—234°, and is decomposed by hydrochloric acid, yielding 5 : 5-diethylbarbituric acid ; the *picrate* has m. p. 190—191°.

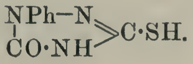
The isomeride, 2-*imino*-4 : 6-*dioxy*-1-*methyl*-5 : 5-*diethylhexahydropyrimidine*,  $\mathrm{NH{:}C}<\begin{matrix}\mathrm{NMe{\cdot}CO}\\ \mathrm{NH{-}CO}\end{matrix}>\mathrm{CEt_2}$, may be prepared by the methylation of 5 : 5-diethylmalonylguanidine ; it has m. p. 187°, and is converted by hydrochloric acid into 1-methyl-5 : 5-diethylbarbituric acid. W. H. G.

Urazoles. XI. Affinity Constants and Constitution of Several Urazoles. SALOMON F. ACREE and G. H. SHADINGER (*Amer. Chem. J.*, 1908, **39**, 124—145).—In an earlier paper (Acree, Abstr., 1907, i, 796), an account was given of the tautomeric relations of phenylurazole and 3-thio-1-phenylurazole, and it was shown that both the 2 : 3- and 4 : 5-amide groups exist in two tautomeric forms in equilibrium, the enolic form preponderating in the former case and the ketonic form in the latter.

The conductivities at 25° have been determined of solutions of phenylurazole, 1-phenyl-2-methylurazole, 1-phenyl-4-methylurazole, 3-thio-1-phenyl-3-methylurazole, and their sodium derivatives, 3-thio-1-phenylurazole and its sodium and barium derivatives, 3-thio-1-phenyl-4-methylurazole, and 3-thio-1-phenyl-3-ethylurazole. Measurements have also been made of the conductivity of solutions of 3-ethoxy-1-phenylurazole, 3 : 5-diethoxy-1-phenylurazole, and 3-ethoxy-1-phenyl-4-methylurazole in $0{\cdot}1N$ alcoholic hydrogen chloride.

The results show that the affinity constant of the 2 : 3-amide group of phenylurazole and of 1-phenyl-4-methylurazole is 0·000011, whilst that of 3-thio-1-phenylurazole and 3-thio-1-phenyl-4-methylurazole is 0·017. The affinity constant of the 4 : 5-amide group of the 2-alkyl and 3-alkyloxy-derivatives of phenylurazole is about 0·00000005, whilst that of the corresponding derivatives of 3-thio-1-phenylurazole is considerably greater.

It is evident therefore that those urazoles which seem to have an enolic structure have much larger affinity constants than those which appear to be ketonic compounds. These results support the view that phenylurazole and 3-thio-1-phenylurazole are tautomeric compounds existing in solution chiefly in the forms  $\begin{matrix}\mathrm{NPh{-}N}\\ \mid\\ \mathrm{CO{\cdot}NH}\end{matrix}\!>\mathrm{C{\cdot}OH}$ and



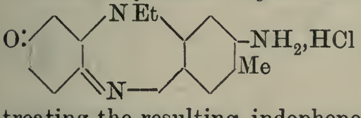
$$\begin{matrix}\mathrm{NPh{-}N}\\ \mid\\ \mathrm{CO{\cdot}NH}\end{matrix}\!>\mathrm{C{\cdot}SH}.$$

E. G.

The Safranines. PHILIPPE BARBIER and PAUL SISLEY (*Ann. Chim. Phys.*, 1908, [viii], 13, 96—142).—A detailed account of work already published (compare Barbier and Vignon, Abstr., 1888, 54, 141, 688; Barbier and Sisley, Abstr., 1905, i, 840; 1906, i, 51, 989; 1907, i, 160, 563; this vol., i, 64). M. A. W.

[Preparation of Safraninones containing Aliphatic Groups.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 189078).—Safraninones containing aliphatic groups are prepared by the further oxidation of the indophenols, obtained either by condensing the nitrosophenols with the 4-alkyltolylene-2 : 4-diamines, or by oxidising a mixture of these bases with the *p*-aminophenols.

Ethotolusafranone hydrochloride (annexed formula) is produced either by condensing nitrosophenol with 4-ethyltolylene-2 : 4-diamine, or by oxidising a mixture of this base and *p*-aminophenol and then treating the resulting indophenol with more oxidising agent.



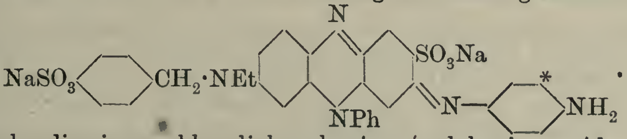
This patent contains a tabulated list of nine of these mixed tolusafraninones, all of which are constituted similarly to the preceding compound. G. T. M.

Preparation of Sulphonic Acids of the Safranine Series. ACTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 186597).—The acylated *p*-diaminoarylphenylaminesulphonic acids,

$$NHAc{\cdot}R{\cdot}NH{\cdot}C_6H_3(NH_2){\cdot}SO_3H,$$

when oxidised in the presence of benzylalkylanilinesulphonic acids, furnish indamines, which on further oxidation with primary aromatic bases give rise to safraninesulphonic acids. Wool dyes are produced by eliminating the acyl group Ac from these safranine derivatives.

Acetyl-*p*-diaminodiphenylaminesulphonic and benzylethylanilinesulphonic acids are treated in aqueous sodium hydroxide with sodium dichromate, and the solution poured into cold 30% acetic acid. The indamine is produced immediately, and subsequently aniline and more dichromate are added. The safraninesulphonic acid thus produced is converted into its sodium salt, which is salted out after filtration from chromic hydroxide. When hydrolysed with moderately dilute sulphuric acid, the foregoing colouring matter is converted into a dye giving greener shades of blue on wool, and having the following constitution:

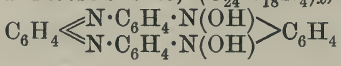


Acetyl-*p*-diamino-*m*-chlorodiphenylamine-*o*′-sulphonic acid, when oxidised successively with benzylethylanilinesulphonic acid and *p*-toluidine, furnishes a safranine which on hydrolysis gives rise to a colouring matter containing a *p*-tolyl group instead of phenyl, and a chlorine atom in the marked position in the foregoing formula. Acetyl-*p*-diaminophenyltolylamine-*o*-sulphonic acid furnishes a safranine of similar constitution, containing a methyl group in the position denoted by the asterisk in the foregoing formula. G. T. M.

Hydrosulphides and Thiohydrosulphides of Dye Bases. Louis Pelet-Jolivet and L. Grand (*Chem. Zentr.*, 1907, ii, 1529; from *Schweiz. Woch. Chem. Pharm.*, 1907, **45**, 375—377).—The action of sodium sulphide on the hydrochlorides of methylene-blue and crystal-violet in concentrated aqueous solution leads to the formation of the *hydrosulphides* of the dye bases, $(C_{16}H_{17}N_3S)_2,H_2S$ and $(C_{25}H_{29}N_3)_2,H_2S$, which are obtained as coloured precipitates. The following *thiohydrosulphides* have been prepared in the same manner by the action of potassium polysulphide on the hydrochlorides of the dyes named: $(C_{16}H_{17}N_3S)_2,H_2S,S_7$ (?), from methylene-blue; $(C_{25}H_{29}N_3)_2,H_2S,S_3$, from crystal-violet; $(C_{22}H_{23}N_3)_2,H_2S,S_4$, from new-magenta; $(C_{23}H_{23}N_2)_2,H_2S,S_7$, from malachite-green; $(C_{33}H_{31}N_3Cl)_2,H_2S,S_5$, from victoria-blue, and $(C_{30}H_{34}O_3N_2)_2,H_2S,S_5$, from anisoline. G. Y.

Relation of Glycine to Uric Acid. Franz Samuely (*Chem. Zentr.*, 1907, ii, 1493; from *Zeitsch. exper. Path. Ther.*, 1907, **4**, 558—560).—Contrary to Hirchstein's statement (*Chem. Zentr.*, 1907, ii, 1181), uric acid does not yield glycine when treated with a dilute alkali. G. Y.

Constitution of Aniline-Black. Fred. Marsden (*J. Soc. Dyers and. Col.*, 1908, **24**, 9—10. Compare Willstätter and Moore, Abstr., 1907, i, 641).—In order to ascertain the quantity of oxygen absorbed in the formation of aniline-black, known quantities of chromic acid were added to a solution of pure aniline hydrochloride, and the action allowed to proceed in the cold until the odour of aniline disappeared; the aniline and chromic acid remaining unchanged were estimated together with the chromium oxide formed. The result obtained was that between 30 and 35 grams of oxygen were used per gram-mol. of aniline. The aniline-black formed had a composition $(C_{12}H_9N_2O)_x$; such a substance can be considered as formed by the polymerisation of Willstätter and Moore's base, $(C_{24}H_{18}N_4)_x$, and the addition of O_2. The structure



$C_6H_4{<}\substack{N\cdot C_6H_4\cdot N(OH)\\ N\cdot C_6H_4\cdot N(OH)}{>}C_6H_4$ is suggested for it.

W. A. D.

[Azo-colouring Matters from the Aminoanilides of the Higher Fatty Acids.] Nathanael Sulzberger (D.R.-P. 188909).—p-*Nitrostearinanilide*, $C_{17}H_{35}\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2$, lemon-yellow, felted needles, m. p. 94·5—95·5°, was obtained by adding nitric acid D 1·17) to a solution of stearinanilide in concentrated sulphuric acid at 50—60° and crystallising from alcohol.

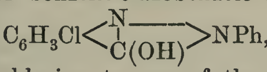
p-*Aminostearinanilide*, $C_{17}H_{35}\cdot CO\cdot NH\cdot C_6H_4\cdot NH_2$, colourless, felted needles, m. p. 118—119°, obtained by reducing the preceding compound in alcoholic solution with iron and acetic acid, when dissolved in alcohol and treated successively at 0° with hydrogen chloride and nitrous fumes or a nitrite, furnishes a stable, colourless *diazo-chloride*, which condenses with alkaline β-naphthol to form a red *azo*-derivative, m. p. 150°, which can be crystallised from chloroform.

Palmitin-β-naphthalide, oleinanilide, and palmitinanilide, when converted successively into nitro- and amino-derivatives, give rise to similar diazo-salts and azo-derivatives; the latter have a combination of fatty and tinctorial properties, which render them of great technical utility. G. T. M.

New Derivatives of *m*-Phenylenetetramethyldiamine. Franz Sachs and Ernst Appenzeller (*Ber.*, 1908, **41**, 109—113).—Azo-dyes, derivatives of chrysoidine, were prepared by coupling freshly-distilled *m*-phenylenetetramethyldiamine, dissolved in dilute acetic acid, with the diazonium chlorides of aniline, *p*-toluidine, β-naphthylamine, and *m*-nitroaniline. Only the *hydrochloride* of m-*nitrobenzeneazo*-m-*phenylenetetramethyldiamine*, $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(NMe_2)_2$, was obtained crystalline in dark violet, matted needles, m. p. 198°. The hydrochloride of *p*-nitroso-*m*-phenylenetetramethyldiamine, prepared by Witt's method (Abstr., 1885, 782; see also Pinnow and Wegener, Abstr., 1898, i, 184), was converted into the free base by cautious addition of sodium hydroxide to the suspension in ice water, and this extracted with ethyl acetate. The purified product forms glistening, greenish-black, prismatic crystals, m. p. 99°, and dissolves with a greenish-yellow coloration. This substance is of interest, as it may be regarded as simultaneously an *o*- and *p*-nitrosoaniline; it can be coupled with methylene and methyl groups to form azomethines. The *picrate* forms dark violet, glistening crystals, m. p. 169°. 2:4-*Bisdimethylaminophenyl-μ-cyano-4′-nitrophenyl-azomethine*,

$$NO_2{\cdot}C_6H_4{\cdot}C(CN){:}N{\cdot}C_6H_3(NMe_2)_2,$$

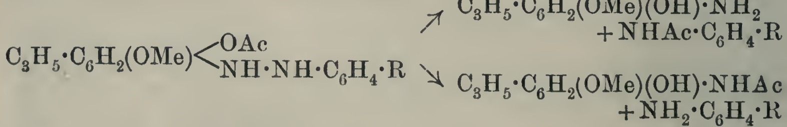
formed by coupling with *p*-nitrophenylacetonitrile, separates in small, glistening, flat plates or fan-like needles, dark red by transmitted and greenish-bronze by reflected light, m. p. 130°. The 2:4-*bisdimethylaminoanil* of 2:4-*dinitrobenzaldehyde*, $C_6H_3(NO_2)_2{\cdot}CH{:}N{\cdot}C_6H_3(NMe_2)_2$, forms violet-red needles with a greenish-bronze lustre, m. p. 209° (decomp.). E. F. A.

Supposed Molecular Transposition in Azo-*o*-carboxylic Acids. Marc Tiffeneau (*Bull. Soc. chim.*, 1907, [iv], **1**, 1201—1205).—It is asserted that Freundler's assumption (Abstr., 1906, i, 544; 1907, i, 158; *Bull. Soc. chim.*, 1907, [iv], 1, 206), that the conversion of benzene-*o*-azobenzoic acid into chloro-3-hydroxy-2-phenylindazole,  $C_6H_3Cl\!<\!\begin{smallmatrix}N\text{———}\\ |\quad\quad\\ C(OH)\end{smallmatrix}\!>\!NPh$, is accompanied by the fixation of an atom of chlorine to one of the nitrogen atoms and its subsequent migration into the nucleus, is unnecessary. The transformation of chloroacetylaniline into *p*-chloroacetanilide by the action of heat (Chattaway and Orton, Trans., 1899, **75**, 1050), quoted by Freundler as an argument in favour of the possibility of this migration, is not strictly analogous, since in this instance the parent substance, acetanilide, contains the group $:NH$, in which the hydrogen atom can be readily replaced by chlorine, whereas in benzene-*o*-azobenzoic acid the corresponding group is $-N{:}H-$, which has never been known to undergo chlorination by the action of phosphorus pentachloride. It is simpler to suppose that the chlorine atom is directly introduced into the nucleus by the action of phosphorus pentachloride, since instances are on record in which this occurs (Henry, *Ber.*, 1869, **2**, 711; Autenrieth and Mühlinghaus, Abstr., 1907, i, 31; Paganini, Abstr., 1891, 556). T. A. H.

Constitution of Azo-compounds. Reply to Tiffeneau. PAUL FREUNDLER (*Bull. Soc. chim.*, 1908, [iv], **3**, 134—139. Compare Abstr., 1906, i, 544; 1907, i, 158).—Polemical. A reply to Tiffeneau (preceding abstract) on the subject of the transformation of *o*-carboxylic azo-compounds into hydroxyindazyl derivatives and the validity of representing supposed intermediate compounds in such transformations by constitutional formulæ. T. A. H.

So-called Mesohydry. KARL AUWERS (*Ber.*, 1908, **41**, 403—415).—In connexion with the conception of mesohydry (compare Oddo and Puxeddu, Abstr., 1905, i, 492; 1906, i, 991; Oddo, *ibid*, 1907, ii, 15), the author has re-examined the derivatives of 5-azoeugenol, and finds that Oddo and Puxeddu's deductions are based on incorrect experimental data. He agrees with these authors in regarding the ethers of the hydroxyazo-compounds as having the azo-structure, and in rejecting the hydrazone formula for the esters, but refutes their arguments against the azo-structure of the latter. Phenolic esters are hydrolysed very easily by phenylhydrazine, and Oddo and Puxeddu's observation that, for example, acetylated benzeneazoeugenol with phenylhydrazine at 110—120° yields aniline and aminoeugenol, does not disprove the fact that the substance is an *O*-ester, but merely shows that hydrolysis has preceded fission. Their second argument, based on the observation that the ethers are hydrolysed by 0·5% sodium hydroxide, whereas the esters are much more stable and consequently cannot have the same structure as the ethers, is quite erroneous; the pure ethers are quite stable, even after being boiled for one hour with 0·5% aqueous or alcoholic sodium hydroxide, whilst under these conditions the acetates are completely hydrolysed.

The author proves that acetylated azoeugenols are *O*-esters by carefully reducing them in alcoholic or ethereal solution by zinc dust and a few drops of acetic acid to hydrazo-compounds, insoluble in alkalis (compare Abstr., 1907, i, 554), which are converted by more vigorous reduction into four fission products, according to the scheme:



$$C_3H_5\cdot C_6H_2(OMe)<\begin{matrix}OAc\\ NH\cdot NH\cdot C_6H_4\cdot R\end{matrix}\ \begin{matrix}\nearrow\ C_3H_5\cdot C_6H_2(OMe)(OH)\cdot NH_2 + NHAc\cdot C_6H_4\cdot R\\ \searrow\ C_3H_5\cdot C_6H_2(OMe)(OH)\cdot NHAc + NH_2\cdot C_6H_4\cdot R\end{matrix}$$

The conception of mesohydry, which is thus shown to be unnecessary in the case of the hydroxyazo-compounds, is also criticised adversely in the other directions in which its originators have applied it.

The new compounds described are: *benzenehydrazoeugenyl acetate*, $C_3H_5\cdot C_6H_2(OMe)(OAc)\cdot NH\cdot NHPh$, m. p. 97°, yellowish-white needles; p-*toluenehydrazoeugenyl acetate*, m. p. 109—110°, softening at 100°;

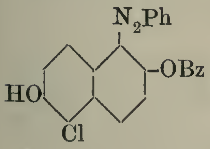
p-*chlorobenzenehydrazoeugenyl acetate*, m. p. 152—154°, white needles; p-*bromobenzeneazoeugenyl ethyl ether*, m. p. 64°, red needles (Oddo and Puxeddu: softens at 68° and m. p. 200°). The m. p. of the preceding hydrazo-compounds, which are readily oxidised, may vary 5° to 10°, according to the rate of heating and to the extent of the previous oxidation.

Oddo and Puxeddu's statement that azoeugenols, which contain a methyl group ortho to the azo-complex, do not form ethers is incorrect in so far as *o*-tolueneazoeugenol is concerned, the *ethyl ether* of which is a red oil. C. S.

Hydroxyazo-compounds. KARL AUWERS and F. EISENLOHR (*Ber.*, 1908, **41**, 415—422).—By condensing benzeneazo-α-naphthol with tetramethyldiaminobenzhydrol, Möhlau and Kegel (Abstr., 1901, i, 56) obtained a substance the acetate of which by reduction yielded acetanilide among other products; hence they concluded that *p*-hydroxyazo-compounds are hydrazones. The authors have repeated the reduction with zinc dust in cold glacial acetic acid, and have failed to detect any trace of acetanilide; aniline, and a substance, probably the acetate of aminonaphthyltetramethyldiaminodiphenylmethane, alone were obtained.

Willstätter and Parnas (Abstr., 1907, i, 1056) have advanced the view that β-benzeneazo-α-naphthol and α-benzeneazo-β-naphthol and their derivatives have different structures, the former being azo-compounds and the latter hydrazones. For this view, they rely solely on the behaviour of the substances on reduction, although several investigators have shown that the reduction of hydroxyazo-compounds is not a safe criterion of structure. The authors have reduced the benzoyl derivatives of the two benzeneazonaphthols with zinc dust and acetic acid; β-benzeneazo-α-naphthyl benzoate yielded aniline, benzanilide, and *N*-benzoyl-2-amino-1-naphthol, whilst α-benzeneazo-β-naphthyl benzoate gave aniline, benzanilide, 1-amino-2-naphthol, and N-*benzoyl*-1-*amino*-2-*naphthol*, m. p. 225°; the last-mentioned substance did not depress the m. p., 232—233°, of a pure specimen obtained by Sachs' method (Abstr., 1906, i, 829). There is therefore no difference in the course of the reduction of the benzoyl derivatives, and consequently no necessity to assume different structures for the parent substances.

Willstätter and Parnas (*loc. cit.*) condensed *as*-benzoylphenylhydrazine and 1 : 5-dichloro-2 : 6-naphthaquinone, and obtained a substance which they formulate as an *N*-benzoylated quinone-hydrazone. Its behaviour on reduction, whereby aniline, benzanilide, and two naphthalene derivatives soluble in alkalis are obtained, shows that the annexed formula is preferable. C. S.



Bisazo-dyes from Phenol and Cresols. GUSTAV SCHULTZ and ERNST ICHENHAEUSER (*J. pr. Chem.*, 1908, [ii], **77**, 100—124. Compare Meyer and Schäfer, Abstr., 1895, i, 135; Meyer and Maier, Abstr., 1903, i, 870).—As little is known of the simple members of the series of bisazo-dyes derived from benzidine, the authors have prepared a number of such substances by coupling diazotised benzidine and tolidine with phenol, the three cresols, and the three phenolsulphonic acids. The resulting bisdiazo-phenols form dialkyl ethers when heated with alkyl haloids and sodium hydroxide, the reaction taking place more readily with benzyl chloride than with ethyl bromide. Sulphonic acids could not be obtained by sulphonation of the benzyl ethers of diphenylbisazo-*o*- and- *m*-cresols. The colorations given with concentrated sulphuric acid by these bisazo-dyes are described.

Diphenylbisazo-o-*cresol*, $C_{12}H_8(N_2\cdot C_6H_3Me\cdot OH)_2$, forms a reddish-brown, crystalline *sodium* derivative, and on reduction yields 4-amino-*o*-cresol, m. p. 170°. The *diethyl ether*, $C_{30}H_{30}O_2N_4$, was analysed; the *dibenzyl ether*, $C_{40}H_{40}O_2N_4$, crystallises in yellowish-red leaflets, m. p. 243°, and on oxidation with potassium chromate and sulphuric acid yields benzoic acid. The m-*cresol dye* and its *sodium* derivative are brown powders; reduction leads to the formation of 4-amino-*m*-cresol. The *diethyl ether* crystallises in yellowish-red needles, m. p. above 200° (decomp.); the *dibenzyl ether*, red leaflets, m. p. 183°. The p-*cresol* derivative is orange-yellow, and on reduction yields 2-amino-*p*-cresol.

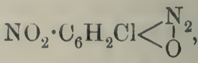
Ditolylbisazophenol, $C_{26}H_{22}O_2N_4$, forms a reddish-brown *sodium* derivative. The *ditolylbisazocresols* are obtained as brown powders on acidification of the alkaline solutions; the solubility in dilute alkalis diminishes from the *o*- to the *p*-cresol derivative. The ditolylbisazophenols dye wool in the same manner as the diphenylbisazophenols, but give stronger shades, which, however, are also not fast to soaping.

Sodium benzyloxybenzene-p-*sulphonate*, $CH_2Ph\cdot O\cdot C_6H_4\cdot SO_3Na$, prepared by heating *p*-phenolsulphonic acid with benzyl chloride in aqueous or alcoholic solution, crystallises in white leaflets. When coupled with diazobenzene chloride in sodium carbonate solution, *p*-phenolsulphonic acid forms the *phenylhydrazone* of *o*-benzoquinonesulphonic acid, $NHPh\cdot N{:}C_6H_3O\cdot SO_3H$, which is obtained in olive-green crystals; the *benzyl ether* forms orange-yellow needles.

The *sodium diphenylbisazophenolsulphonates*, $C_{24}H_{16}O_8N_4S_2Na_2$, prepared by coupling diazotised benzidine with *o*-, *m*-, and *p*-phenolsulphonic acid in sodium carbonate solution, and the corresponding *compounds*, $C_{26}H_{20}O_8N_4S_2Na_2$, prepared from diazotised tolidine, form brown or red powders. The *dibenzyl ethers* form orange-yellow, red, or brown powders. These sodium salts readily dye vegetable fibres, but the dyeings are not fast to soaping. G. Y.

[4-Chloro-5-nitro-2-aminophenol and its Diazo-oxide.]

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 186655).—4-*Chloro-5-nitro-2-aminophenol*, needles, m. p. 225°, obtained together with 4-chloro-6-nitro-2-aminophenol on nitrating 4-chloro-2-aminophenol, is also produced by the nitration of the ethenyl derivative of 4-chloro-2-aminophenol and the subsequent hydrolysis of the nitro-compound.



4-*Chloro-5-nitro-*1:2-*phenylenediazo-oxide*, $NO_2\cdot C_6H_2Cl{<}\genfrac{}{}{0pt}{}{N_2}{\overset{|}{O}}$, separates in yellowish-red crystals on diazotising the foregoing aminophenol; it combines in alkaline solution with various naphthol- and dihydroxynaphthalene-sulphonic acids to furnish a series of hydroxyazo-dyes which yield varying shades of blue on chrome-mordanted wool.

G. T. M.

Preparation of Salts of 1-Diazo-β-naphtholsulphonic Acids. Badische Anilin- & Soda-Fabrik (D.R.-P. 189179. Compare Abstr., 1906, i, 907).—It has now been found that the free 1-amino-β-naphtholsulphonic acids may be readily and quantitatively diazotised in aqueous solution with sodium nitrite in the presence of a salt of ammonium or the alkali or alkaline earth metals. A mixture of 1-amino-β-naphthol-4-sulphonic acid with a solution of sodium nitrite and chloride gradually changes to a clear brownish-yellow solution, from which sodium 1-diazo-2-oxynaphthalene-4-sulphonate slowly separates in yellow needles.

G. T. M.

Deaminoedestin. Walter Traxl (*Monatsh.*, 1908, **29**, 59—68).—Skraup and his co-workers have shown that the deamino-proteins differ from the proteins from which they are formed by the action of nitrous acid in that on hydrolysis they do not yield lysine. This is now found to be the case also with deaminoedestin, which differs from edestin also in other properties. As the average value of several analyses, edestin is found to contain N = 18·92%, and deaminoedestin, N = 19·62%; this increase in the percentage of nitrogen does not result from the formation of a nitroso-derivative and remains unexplained. On hydrolysis, deaminoedestin yields 1·7—2·18% of histidine and 1·5% of arginine, whereas edestin yields about 12% of arginine and 2% of histidine.

G. Y.

Leucine from Casein. Fritz Heckel (*Monatsh.*, 1908, **29**, 15—21).—The formation of *n*-valeric acid by the action of bromine on casein (Skraup and Witt, Abstr., 1906, i, 916) suggests the presence of *n*-leucine in casein. In agreement with this, it is found that, on oxidation with potassium permanganate, the leucine from the least soluble hydrochloride fraction of the hydrolysis products of casein yields a mixture of acids about one-half of which is *n*-valeric acid. Hence the leucine from casein must contain small amounts of α-amino-*n*-hexoic acid.

G. Y.

Leucine from the Ligamentum Nuchæ of Oxen. Maximilian Samec (*Monatsh.*, 1908, **29**, 55—58).—Leucine obtained from the ligamentum nuchæ of oxen (Erlenmeyer and Schäffer, *Zeitsch. Chem. Pharm.*, **59**, 315) probably contains *n*-leucine, as on oxidation with permanganate it yields *n*-valeric acid (Heckel, preceding abstract). When treated with hydrogen iodide as described by Kwisda (Abstr., 1892, 38), the leucine yields much inflammable gas, and only small amounts of acids volatile with steam.

G. Y.

Hæmins. J. Merunowicz and Jean Zaleski (*Bull. Acad. Sci. Cracow*, 1907, 633—646).—The crystalline hæmin, which Nencki and Zaleski first obtained by direct extraction of coagulated blood corpuscles with acetone (Abstr., 1900, i, 709), is now shown to be a molecular compound of hæmin with acetone, *acetonehæmin* (most probably $C_{34}H_{32}O_4N_4ClFe,COMe_2$). A simple method for its preparation is described in detail; it cannot be recrystallised as such, but can readily be transformed into Teichmann's crystals by allowing its solution in ammonia to flow into acetic acid saturated with sodium chloride. If a bromide or an iodide is used instead of a chloride in the recrystallisation of Teichmann's crystals, other hæmins are obtained, *bromohæmin*, $C_{34}H_{32}O_4N_4BrFe$, and *iodohæmin*,

$$C_{34}H_{32}O_4N_4IFe.$$

The spectroscopic behaviour and general properties of the three hæmins are very similar. The one containing iodine is somewhat less soluble than the others, and forms unusually large crystals (up to 2 mm.). G. B.

Blood Pigment. VIII. LEON MARCHLEWSKI and J. RETTINGER (*Zeitsch. physiol. Chem.*, 1907, **54**, 151—152. Compare Abstr., 1907, i, 738).—The main product of the action of diazobenzene chloride on hæmopyrrole in an ethereal solution is *benzenebisazomethylpropylpyrrole.* From the mother liquor, after the precipitation of this compound, ruby-red crystals of a second substance are obtained on concentration; on further concentration, a third substance in green, badly formed crystals is obtainable. The spectroscopic appearances of these substances are described. W. D. H.

The Fundamental Colouring Matter of Urine. STEPHANE DABROWSKI (*Bull. Acad. Sci. Cracow*, 1907, 777—836).—The use of fixed alkali in the preparation of urochrome was found to be inadmissible, since part of the sulphur contained in this substance is readily eliminated. The method employed finally in the preparation was as follows: to 1500 c.c. of urine a solution of 18 grams of calcium acetate and of 8 grams of barium acetate was added, and then 6·5 c.c. of 21% ammonia. After filtration, the filtrate was neutralised with acetic acid, the urochrome was then precipitated by the addition of cupric acetate, and purified by successive transformation into the barium, sodium, and silver salts. Urochrome is an acid the silver salt of which yields with methyl iodide a methyl ester. Reduced with phosphonium iodide, urochrome does not yield hæmopyrrole, and is therefore not connected with urobilin. It contains, however, a simple pyrrole nucleus, as shown by the pinewood reaction of the distillate obtained by heating urochrome with lime. The absorption spectrum of this distillate closely resembles the spectrum of pyrrole which has undergone spontaneous polymerisation on keeping, and is different from that of urobilin.

Sixty-eight per cent. of the sulphur contained in urochrome is readily eliminated by boiling alkali, and can be estimated as lead sulphide.

Urochrome can be (roughly) estimated in urine by subtracting the amount of purine nitrogen, obtained according to Huppert's modification of Haycraft's ammoniacal silver nitrate method, from the amount found by Krüger and Wulff's cuprous sulphate method; the difference between the two values represents the nitrogen in urochrome, of which 0·4—0·7 gram are excreted daily by man.

The author does not admit the relationship between urochrome and bilirubin, which exists according to Garrod (Abstr., 1903, ii, 520). Not only does urochrome not yield hæmopyrrole, but it contains sulphur, and has a very different elementary composition from that of urobilin (C 43·09%, H 5·14%, N 11·15%, S 5·09%). G. B.

Physical Modifications of Gelatin in the Presence of Electrolytes and Non-electrolytes. J. Larguier des Bancels (*Compt. rend.*, 1908, **146**, 290—291).—Sadikoff (Abstr., 1904, i, 462; 1906, i, 224) has shown that gelatin dissolves in very concentrated solutions of certain salts. The author has studied the solvent action of 2*M*-solutions of the nitrates and chlorides of sodium, potassium, ammonium, calcium, magnesium, zinc, copper, and manganese on rectangular fragments of gelatin, and finds that the salts of the bivalent metals have a greater action than those of the univalent metals, those of calcium having the greatest activity, and that the nitrates are generally more active than the chlorides.

In the presence of electrolytes, particularly the above salts, gelatin dissolves in mixtures of water with methyl or ethyl alcohol or acetone more readily than in pure water. The presence of a small quantity of water is essential for dissolution, but, apart from this, the gelatin dissolves the more rapidly the larger the quantity of non-electrolyte present.

The gelatin so dissolved can be recovered by eliminating the salts from solution, either by dialysis or by a series of precipitations.

E. H.

Tanning of Gelatin. Richard Abegg and Paul von Schroeder (*Chem. Zentr.*, 1907, ii, 1346—1347; from *Zeitsch. Chem. Ind. Kolloide*, 1907, **2**, 85—87).—As a measure of the extent to which gelatin has been tanned, the authors use the temperature of fusion, which is the temperature at which the gelatin begins to flow in a thin-walled, open glass tube, 2·5 mm. in diameter and 2·5 cm. in length.

A 10% (solid) solution of gelatin, covered with 5% formalin, is kept for twenty-four hours. The surface layer of gelatin, which is strongly tanned, shrivels and darkens at 85° without melting; the following layers have m. p. 48° to 36°. The m. p. of the untanned gelatin is 36°.

Experiments with gelatin plates show that a definite degree of tanning, namely, that corresponding with m. p. 48°, is reached in a time which is nearly inversely proportional to the concentration of the formalin; at very small concentrations, however, the degree of tanning is less than the calculated amount. The process is a unimolecular reaction, the concentration of the gelatin being taken as constant.

The tanning action of 1% formalin is not affected by the presence of 20(vol.)% alcohol. A depression of the m. p. of gelatin to 34° and 32°, without visible tanning, is caused by 10% solutions of potash and chrome alums respectively; ferric alum, however, produces a hard, brittle gelatin, m. p. 40—38°. Successive treatment in baths of potassium dichromate and sodium thiosulphate, and also solutions of tannin or picric acid, tan gelatin with lowering of the m. p.

The m. p. of untanned gelatin is lowered by neutral salts; the action also occurs with tanned gelatin, for, whereas the m. p. of untanned gelatin is lowered to 33° in a bath of sodium chloride, the m. p. (41°) of a tanned gelatin is depressed to 38°. The addition of sodium carbonate causes a rapid acceleration of the tanning action of formalin or ferric alum with simultaneous elevation of the m. p. of the gelatin.

The internal friction of a dilute solution of gelatin diminishes with time after the addition of formalin; by the addition of potash or chrome alums, it increases to an extent approximately equal to that which the same quantity of water would experience by the addition of these salts. C. S.

Isolation of Glycine, Albumoses, or Peptones from Dilute Aqueous Solutions. MAX SIEGFRIED (D.R.-P. 188005).—Glycine, albumoses, and peptones may be precipitated with the formation of a complex carbamate by suspending barium or strontium hydroxide in their solutions and passing in carbon dioxide. The precipitate is then warmed with water containing carbon dioxide or ammonium carbonate in order to form calcium carbonate and the free amino-acid.

G. T. M.

Plastein. W. W. SAWJALOFF (*Zeitsch. physiol. Chem.*, 1907, **54**, 119—150).—Plastein is the name given to the precipitate which is obtained when solutions of proteoses are subjected to the action of gastric juice. The material is obtained from different kinds of proteose, and the process is regarded as a synthetic one (reversible action of pepsin). By the further digestion of plastein, the usual varieties of proteose and peptone are obtained. The figures given indicate that the reaction is either bimolecular or termolecular; plastein is therefore the result of the union of either 2 or 3 molecules of the proteoses from which it is formed, and its molecular weight is, on the average, twice that of the proteoses. Before precipitation occurs, plastein is present in a soluble form, and is then precipitated by boiling. The plasteins used were prepared from a large range of proteins, and elementary analyses are given. They differ among themselves, and are divided into groups. W. D. H.

Protagon. WILHELM CRAMER and R. A. WILSON (*Quart. J. Exp. Physiol.*, 1908, **1**, 97—110).—Polemical. The individuality of protagon is maintained, and the statements of Gies and his collaborators and of Rosenheim and Miss Tebb criticised. W. D. H.

A Simple Method of Estimating the Activity of Trypsin. OSCAR GROSS (*Arch. expt. Path. Pharm.*, 1907, **58**, 157—166).—The method is based on the fact that caseinogen is precipitated from alkaline solution by the addition of acid, but that the products of its digestion are not precipitated. The moment is noted at which the digesting solution ceases to give a precipitate on acidification with 1% acetic acid. It is found experimentally that the time required for digestion is inversely proportional to the amount of trypsin employed, so that tryptic digestion does not follow the Schütz-Borissow law of squares, which applies to peptic digestion only. G. B.

Adsorption Affinity of Invertase from Yeast. Leonor Michaelis (*Biochem. Zeitsch.*, 1908, 7, 488—492).—The behaviour of invertase from yeast towards kaolin, mastic, arsenious sulphide, ferric hydroxide, and aluminium hydroxide indicates that the enzyme is an electronegative colloid. The precipitate, consisting of ferric hydroxide or aluminium hydroxide, and the adsorbed ferment is as active as an aqueous solution of invertase. A solution containing both albumin and invertase can be freed from the former by means of kaolin. The filtrate from the kaolin and adsorbed albumin contains the invertase. J. J. S.

The Inhibiting Action of Fluorides on Lipase. Samuel Amberg and Arthur S. Loevenhart (*J. Biol. Chem.*, 1908, 4, 149—164). —The inhibiting action of fluoride on lipase decreases on ascending the fatty acid series of esters. The accelerating effect of sodium salts of the fatty acids neutralises the effect of a fluoride. For this purpose, sodium butyrate must be present in a molecular concentration 2100 times as great as that of the fluoride. The action of the sodium salts decreases with increasing molecular weight of the salt, and the protecting action increases with the increasing molecular weight of the ester. The effect of fluorides furnishes a biochemical test for fluorides in food products, and this will doubtless be of value in food inspection. W. D. H.

The Fermentative Change of Glyoxylic Acid in Organs. E. Granström (*Beitr. chem. Physiol. Path.*, 1908, 11, 214—223).—Schloss showed that, of various organs, the liver (minced small) was most effective in causing the disappearance of glyoxylic acid. The property is possessed by extracts of liver made with Ringer's solution, and to a less degree by the precipitate produced by alcohol or acetone in such extracts. Evidence is adduced that the agent is a ferment, and the name *glyoxylase* is given to it. It is relatively resistant towards acids, alkalis, and antiseptics, and its activity is destroyed by heating. It acts in the absence of oxygen; its action is not oxidative, no oxalic acid being formed. The ferment is not identical with aldehydase, or with the uricolytic enzyme. It does not pass through a Chamberland filter. W. D. H.

An Enzyme Phytase which Decomposes Anhydro-oxymethylenediphosphoric Acid. Umetaro Suzuki, K. Yoshimura, and M. Takaishi (*Bull. Coll. Agric. Tokyo*, 1907, 7, 503—512).—When rice bran suspended in water is kept for some days at the ordinary temperature, most of the organic phosphorus dissolves, and phosphoric acid is produced at the expense of the organic phosphorus compounds. The change is shown to be due, not to putrefaction, but to an enzyme, phytase, which was isolated from rice bran and wheat bran. The enzyme dissolves very readily in cold water, is free from phosphorus, and does not possess either diastatic, peptic, or tryptic activity.

The production of inositol from phytin, which has hitherto only been effected by means of strong mineral acid, is also brought about by phytase. It is therefore probable that phytin has the constitution of inositol-hexaphosphoric acid, $C_6H_6(PO_4H_2)_6$. N. H. J. M.

The Probable Chemical Constitution of Rennet. ALBERTO SCALA (*Chem. Zentr.*, 1907, ii, 1800; from *Staz. sperim. agrar. ital.*, **40**, 129—149).—Rennin is regarded as a weak base, consisting of an albumose nucleus and amino-side-chains. Heating destroys its activity, and alters its constitution; formaldehyde has a similar action, which is explained by the replacement of amide-hydrogen by the methylene group. W. D. H.

Pepsin and Rennet. IVAR BANG (*Zeitsch. physiol. Chem.*, 1908, **54**, 359—362).—The view is taken that these two substances are not identical, and Gewin's results (this vol., i, 71) are criticised.

W. D. H.

Ferments and Antiferments. VI. MARTIN JACOBY (*Biochem. Zeitsch.*, 1908, **8**, 40—41. Compare Abstr., 1907, i, 811; ii, 38, 108).—Morgenroth and Willanen (*Virchow's Archiv*, 1907, **190**) have questioned the accuracy of the author's observation (Abstr., 1907, ii, 38) that a neutral mixture of rennet and antirennet can be re-activated by the addition of acid. They doubted the activity of the antiferment, and regarded the clotting action after acidification as due to liberation of fresh rennet from (as yet undecomposed) zymogen, or as due to the intensification, by the acid, of the action of traces of rennet which had escaped neutralisation by the antirennet. The reply to these criticisms is that the experiments with antirennet were carried out quantitatively, so that its activity was beyond suspicion; moreover, it was always present in such excess that it would have sufficed to neutralise the rennet several times over. G. B.

Action of Tyrosinase on some Substances Related to Tyrosine. GABRIEL BERTRAND (*Compt. rend.*, 1907, **145**, 1352—1355).—In view of extending the study of tyrosinase as a melanogenetic oxydase (compare Abstr., 1896, ii, 571; 1897, ii, 117, 338; Gessard, Abstr., 1900, i, 468; 1902, i, 196; 1903, ii, 165; 1904, i, 539; ii, 833; Lehmann, Abstr., 1902, i, 580; Fürth and Schneider, Abstr., 1902, ii, 36; Cotte, Abstr., 1903, ii, 309; Durham, Abstr., 1905, ii, 101), the author has examined the action of the pure oxydase (Bertrand and Mutermilch, Abstr., 1907, i, 812) on two series of compounds related to tyrosine; the first series includes phenol and its para-substituted derivatives, ethyltyrosine, chloroacetyltyrosine, glycyltyrosine, tyrosine, *p*-hydroxyphenylethylamine, *p*-hydroxyphenylmethylamine, *p*-aminophenol, *p*-hydroxyphenylpropionic acid, *p*-hydroxyphenylacetic acid, *p*-hydroxybenzoic acid, and *p*-cresol. The second series comprises phenylalanine, phenylethylamine, phenylmethylamine, anilinoacetic acid, phenylpropionic acid, phenylacetic acid, alanine, and glycine. The results show that, whilst each member of the first series of compounds is oxidised by tyrosinase to form intensely coloured derivatives, those of the second series yield no coloration under the same conditions; it follows therefore that only those compounds containing the phenolic hydroxyl group are susceptible to the oxidising action of tyrosinase.

The dipeptide glycyltyrosine is not hydrolysed by tyrosinase, neither is it oxidised by laccase. M. A. W.

The Action of Tyrosinase from Russula delica on Tyrosine, Tyrosine-containing Polypeptides, and other Compounds. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Zeitsch. physiol. Chem.*, 1908, **54**, 331—353).—The presence of *d*-glutamic and *l*-aspartic acids inhibits the formation of pigment from tyrosine under the influence of tyrosinase. Numerous other amino-acids have no such effect. Various alcohols are also without inhibiting influence. Details are given in regard to the influence of various agencies on the similar action of tyrosinase on polypeptides which contain tyrosine. Tyrosinase produces a red pigment from polypeptides which contain tryptophan, and this is not due to comtamination with tyrosine. W. D. H.

Peroxydase Active in Tyrosinase. ALEXIS BACH (*Ber.*, 1908, **41**, 216—220. Compare Abstr., 1906, 616, 919).—Tyrosinase consists of an oxygenase for which hydrogen peroxide can be substituted and a peroxydase. Chodat's observation (Abstr., 1907, i, 575, 882) that hydrogen peroxide retards the activity of tyrosinase is due to the use of too concentrated solutions; in suitable dilution, hydrogen peroxide has no influence on the activity of fresh normal tyrosinase. Here it would appear the peroxide produced by the oxygenase is sufficient for the requirements of the corresponding peroxydase. The action of vegetable tyrosinase on tyrosine may be followed quantitatively by decolorising the black oxidation product produced with dilute potassium permanganate and sulphuric acid.

Older and partly exhausted preparations of tyrosinase have their action considerably accelerated on addition of dilute hydrogen peroxide, and a preparation which had entirely lost its activity was rendered very active again in this manner. Seemingly, the oxygenase is very unstable, but it can be completely replaced by the corresponding amount of hydrogen peroxide.

By precipitation with magnesium carbonate and extraction of the dried precipitate with water, the peroxydase may be partly separated from the oxygenase, the magnesium carbonate retaining very much more of the former. A similar partial separation is also effected by methyl alcohol. E. F. A.

Mode of Action of Tyrosinase. ALEXIS BACH (*Ber.*, 1908, **41**, 221—225).—Tyrosinase derived from *Russula delica* was allowed to act on tyrosine in dilute sodium carbonate, and the amount of change determined by titration with potassium permanganate and sulphuric acid (see preceding abstract). The course of change follows the simple law of mass action. The amount changed increases with, although more slowly than, the amount of ferment, and the reaction comes more quickly to a standstill the larger the amount of ferment. With a constant amount of ferment during the middle portion of the reaction, the time taken for a given amount of change is inversely proportional to the amount of tyrosine present. The activity of the ferment is the more rapidly exhausted as the amount of tyrosine present increases. E. F. A.

Behaviour of Peroxydase towards Light. Alexis Bach (*Ber.*, 1908, **41**, 225. Compare Abstr., 1907, i, 268).—Under the combined influence of oxygen and of light, there is a slow falling off in the activity of peroxydase as measured by the production of purpurogallin from pyrogallol. Generally speaking, peroxydase appears to be one of the most stable enzymes. E. F. A.

Amount of Nitrogen in the Oxidising Ferments. Alexis Bach (*Ber.*, 1908, **41**, 226—227).—Peroxydase from horse-radish, when heated with powdered potassium hydroxide, yields pyrrole and ammonia. In detecting nitrogen in oxidising ferments by the Lassaigne method, it is advisable to use a fair proportion of metallic potassium and not sodium. E. F. A.

The Enzymic Rôle of Philothion towards Oxygen. Joseph de Rey-Pailhade (*Bull. Soc. chim.*, 1908, [iv], 3, 159—162. Compare Abstr., 1906, i, 999; 1907, i, 372; 1908, i, 72).—Lambling's statement (*Dict. Chim. de Wurtz*, article "Philothion") that the enzymic nature of philothion is doubtful has led the author to summarise the information he has already brought forward in favour of regarding this substance as an enzyme, and he concludes that its function in the living processes is to hydrogenate oxygen, and that it behaves as an enzyme towards oxygen in this connexion.

T. A. H.

Cleavage of Polypeptides. Emil Abderhalden and Arthur H. Koelker (*Zeitsch. physiol. Chem.*, 1908, **54**, 363—389).—In a previous research on the hydrolysis of *d*-alanyl-*d*-alanine by means of yeast-juice (Abstr., 1907, ii, 488), the amount of the dipeptide was kept constant, and the amount of ferment was varied. In the present research, the constant quantity was the amount of ferment, and the variable one the amount of dipeptide. The tabular results and curves given show that the greater the amount of ferment in proportion to dipeptide the more rapidly did hydrolysis take place, especially at the start.

The next experiments relate to the action of pancreatic and intestinal juice on certain tripeptides, namely, *l*-leucyl-glycyl-*d*-alanine and glycyl-*d*-alanyl-glycine. The specific rotatory power of the former is +20°. By hydrolysis, it is theoretically possible to obtain two dipeptides, namely, *l*-leucyl-glycine and glycyl-*d*-alanine; the rotatory power of the former is +85°, of the latter −50°. So that if leucine is liberated, the rotation will sink, and if *d*-alanine is liberated the rotation will rise. With the second tripeptide, an examination of the rotatory power will also indicate the course of the hydrolysis, for its rotatory power is −64°, and that of the two possible dipeptides −50° and +50°. The results show in the case of *l*-leucyl-glycyl-*d*-alanine, the main reaction is the formation of alanine and *l*-leucyl-glycine, and this dipeptide is in small measure resolved into leucine and glycine. In the case of glycyl-*d*-alanyl-glycine, the first cleavage results in the liberation of glycine and *d*-alanyl-glycine.

The next series of experiments relate to the influence of alkalis and acids on the cleavage which pancreatic and intestinal juice produce on glycyl-*l*-tyrosine. Small quantities of alkali retard hydrolysis. The same is true for the action of yeast-juice on *d*-alanyl-*d*-alanine. Even small quantities of acid completely inhibit the hydrolysis. The results with bile acids are inconclusive. W. D. H.

Sensitising Action of Fluorescent Substances in Yeast and Yeast Press Juice. HERMANN VON TAPPEINER, M. KURZMANN, and FR. LOCHER (*Biochem. Zeitsch.*, 1908, **8**, 47—60. Compare Abstr., 1904, i, 131; 1905, ii, 565, 602, 603; 1906, i, 720, 917; ii, 462, 511, 512; 1907, i, 267).—Fluorescent substances can in diffuse daylight inhibit yeast fermentation, and even kill the yeast. Certain fluorescent substances, such as sodium dichloroanthracenedisulphonate, which act strongly on *Paramœcium*, are without action on yeast. On the other hand, all fluorescent substances examined greatly inhibited the fermentative action of yeast-juice (zymase) and of dead yeast preserved by acetone. This destructive action on intra-cellular enzymes is similar to that on extra-cellular ones. It would seem therefore that some fluorescent substances, like sodium dichloroanthracenedisulphonate, referred to above, cannot pass through the cell wall.

G. B.

Action of Light on Peroxydase; Sensitisation by Fluorescent Substances. KANDO JAMADA and ALB. JODLBAUER (*Biochem. Zeitsch.*, 1908, **8**, 61—83). **Sensitisation of Catalase.** M. ZELLER and ALB. JODLBAUER (*Biochem. Zeitsch.*, 1908, **8**, 84—97). —Peroxydase and catalase are attacked by visible rays in the presence of oxygen, and by ultra-violet rays to an even greater extent, no matter whether oxygen is, or is not, present. Catalase is rendered more susceptible to the light by the presence of hydroxyl ions. All fluorescent substances examined sensitised catalase, but peroxydase was only sensitised by eosin and by tetrabromotetraiodofluorescein. The sensitising action only occurs when the ultra-violet rays are as far as possible absent, and is small compared with the similar action on diastase and invertase. (Compare the references given in the preceding abstract.) G. B.

Isomeric Organic Magnesium Compounds. JULIUS SCHMIDLIN and HERBERT H. HODGSON (*Ber.*, 1908, **41**, 430—437. Compare Abstr., 1907, i, 26, 601).—Cinnamaldehyde reacts in a similar manner to benzaldehyde with the α- and β-forms of magnesium triphenylmethyl chloride. An ethereal solution of the α-isomeride is prepared in the usual way, and, after the evaporation of the greater part of the ether, the precipitated magnesium compound is re-dissolved by the addition of dry benzene; the addition of cinnamaldehyde leads to the formation of p-*cinnamoyltriphenylmethane*, $CHPh_2\cdot C_6H_4\cdot CO\cdot CH\colon CHPh$, m. p. 149—151° (corr.), which develops a yellow coloration with concentrated sulphuric acid. The formation of the ketone instead of a secondary alcohol is due probably to atmospheric oxidation. An ethyl ether-benzene solution of β-magnesium triphenylmethyl chloride reacts with cinnamaldehyde to form *cinnamoyltriphenylmethane*,

$$CPh_3\cdot CO\cdot CH\colon CHPh,$$

m. p. 159—160° (corr.), which does not develop a coloration with concentrated sulphuric acid.

Benzyl chloride reacts very feebly with the α-form of magnesium triphenylmethyl chloride, yielding a trace of *as*-tetraphenylethane; with the β-isomeride, however, it readily forms the same hydrocarbon (compare Hanriot and St. Pierre, Abstr., 1889, 882; Gomberg, *ibid.*, 1906, i, 821.)

The α- and β-forms of magnesium triphenylmethyl chloride yield β-benzpinacolin with methyl benzoate, and do not react with acetone, acetaldehyde, or acetyl chloride, although in the case of the β-isomeride minute traces of triphenylmethyl are formed. *m*-Nitrobenzaldehyde does not react with the β-form, and converts the α-isomeride largely into triphenylcarbinol.

p-Tritolylmethyl chloride loses hydrogen chloride at 180—250°, yielding an amorphous powder, m. p. 225—235°, which is possibly ditolylenetolylmethane (tolyldimethylfluorene), $C_{22}H_{20}$.

Magnesium p-*tritolylmethyl chloride* appears to be formed as a yellow precipitate when magnesium and *p*-tritolylmethyl chloride react in ether in the presence of excess of iodine or bromine. It reacts with benzaldehyde to form an amorphous *hydrocarbon*, $C_{29}H_{26}$, m. p. 195—200°, but does not yield tritolylacetic acid with carbon dioxide. The acid is formed, however, when carbon dioxide is passed into the ethereal solution in which magnesium and tritolylmethyl chloride are reacting in the presence of a smaller quantity of iodine than that used in the preceding preparation. C. S.

Organic Chemistry.

Presence of two Paraffin Hydrocarbons in the Unsaponifiable Portion of Chrysalidene Oil. ANGELO MENOZZI and A. MORESCHI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 100—101. Compare Lewkowitsch, Abstr., 1907, i, 521).—The portion of chrysalidene oil which cannot be saponified consists of: (1) bombicesterol (compare this vol., i, 265); (2) a product which dissolves readily in alcohol or ether, and separates as a varnish; (3) a saturated, optically inactive hydrocarbon, $C_{28}H_{58}$, m. p. 62·5°, b. p. 270°/15 mm. (compare Krafft, *Chem. Zeit.*, 1883, 153); (4) a saturated *hydrocarbon*, m. p. 41—42°).

T. H. P.

Action of Nitric Acid on Saturated Hydrocarbons. XIII. Nitration of Saturated Hydrocarbons containing two *iso*Propyl Groups. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 1119—1125. Compare Abstr., 1905, i, 762, 763, 764).—By the action of nitric acid on American petroleum, b. p. 55—60°, β-nitro-βγ-dimethylbutane, $NO_2·CMe_2·CHMe_2$, b. p. 168—169°/750 mm., is obtained amongst other products; it is either identical or closely analogous to the substance obtained by the nitration of synthetic di*iso*propyl (βγ-dimethylbutane), has D_0^0 0·9716, D_0^{20} 0·9588, crystallises in a mixture of solid carbon dioxide and ether, and melts below −20° (compare Abstr., 1894, i, 265).

It is reduced by tin and hydrochloric acid, forming the corresponding *amine*, b. p. 104—105°/751 mm., D_0^0 0·7683, D_0^{27} 0·7514, n_D^{17} 1·40960, and does not solidify at −9°. It readily absorbs carbon dioxide from the atmosphere, forming a solid *salt*; the *hydrochloride* of the amine is readily converted into dimethyl*iso*propylcarbinol, $CHMe_2·CMe_2·OH$. Simultaneously with the mononitro-compound, βγ-dinitro-βγ-dimethylbutane, b. p. 208°, is formed.

Amongst other products obtained by nitrating βδ-dimethylpentane with nitric acid, D 1·11, in sealed tubes are: (1) *β-nitro-βδ-dimethylpentane*, $NO_2·CMe_2·CH_2·CHMe_2$, b. p. 181—182°/742 mm., D_0^0 0·9559, D_0^{30} 0·9309, n_D^{30} 1·42355, which is reduced by tin and hydrochloric acid, forming the corresponding *amine*, b. p. 121—122°/747 mm., D_0^{30} 0·7549, n_D^{30} 1·4009; the *platinichloride*, m. p. 240° (decomp.), is described.

(2) *βδ-Dinitro-βδ-dimethylpentane*, $NO_2·CMe_2·CH_2·CMe_2·NO_2$, is a crystalline substance, m. p. 81—82°.

Z. K.

A New Type of Combination of Sulphur with Certain Iodides. VICTOR AUGER (*Compt. rend.*, 1908, 146, 477—479).—The author has prepared a new series of additive or molecular compounds of the type RI_n,nS_8 by mixing solutions in carbon disulphide of the two constituents. *Iodoform-sulphur*, $CHI_3,3S_8$, forms magnificent yellow prisms, m. p. 93°, stable in air, but coloured red by the action of light. *Tetraiodoethylene-sulphur*, $CI_2{:}CI_2,4S_8$, form large, yellow plates, m. p. 97—103°. *Arsenious iodide-sulphur*, $AsI_3,3S_8$, forms long, orange prisms or plates, m. p. 105°. *Antimony iodide-sulphur*, $SbI_3,3S_8$, forms long, bright yellow prisms, m. p. 117°.

M. A. W.

Reducing Properties of the Organometallic Compounds. LETELLIER (*Compt. rend.*, 1908, **146**, 343—345. Compare Jocitsch, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 443; Sabatier and Mailhe, Abstr., 1905, i, 706; Gattermann and Maffezzoli, Abstr., 1904, i, 172).—When ethyl hydroxypivalate, $OH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2Et$, is treated with magnesium ethyl bromide, besides the production of *ββ-dimethyl-γ-ethylpentane-αγ-diol*, $OH{\cdot}CH_2{\cdot}CMe_2{\cdot}CEt_2{\cdot}OH$, m. p. 19°, b. p. 136°/21 mm., predicted by theory, there is formed a smaller quantity of *ββ-dimethylpentane-αγ-diol*, $CH_2Me{\cdot}CH(OH){\cdot}CMe_2{\cdot}CH_2{\cdot}OH$, m. p. 59°, b. p. 119°/21 mm., identified by its production when ethyl bromo*iso*butyrate is condensed with propaldehyde in the presence of zinc (Reformatski) and the *ethyl β-hydroxy-αα-dimethylvalerate*,

$$CH_2Me{\cdot}CH(OH){\cdot}CMe_2{\cdot}CO_2Et$$

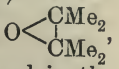
(b. p. 98°/16 mm.), so formed, reduced by sodium (Bouveault and Blanc, Abstr., 1905, i, 11). The mechanism of the formation of the second glycol is represented by $OH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2Et + MgEtBr \longrightarrow OH{\cdot}CH_2{\cdot}CMe_2{\cdot}CEt(OEt){\cdot}OMgBr \longrightarrow OH{\cdot}CH_2{\cdot}CMe_2{\cdot}COEt$, the ketone formed being reduced by the organometallic compound with evolution of ethylene. Lowering the temperature of the reaction-mixture favours the reduction, the yield of the second glycol being 32% at the ordinary temperature, 35% at 0°, and 60% in a mixture of ice and salt. The first glycol, which forms an *acetate*, b. p. 97—98°/21 mm., and a *urethane*, m. p. 63°, is dehydrated by 20% sulphuric acid, giving *ββ-dimethyl-γ-ethyl-$\Delta^{\gamma\delta}$-pentenol*, $CHMe{:}CEt{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$, a liquid, b. p. 86°/21 mm., and a small quantity of a liquid *hydrocarbon*, b. p. 119°, probably a nonane. The second glycol, which cannot be dehydrated, forms an *acetate*, b. p. 116°/21 mm.

E. H.

General Method for the Preparation of Fatty or Aromatic Primary Ethers. JULES L. HAMONET (*Bull. Soc. chim.*, 1908, [iv], 3, 254—258).—In view of the publication of Reychler's papers (this vol., i, 158, 159) describing the preparation of complex ethers by the action of chlorodimethyl ether on magnesium alkyl haloids, the author calls attention to the fact that he has already described this reaction (Abstr., 1904, i, 401), and indicated that it is capable of general application.

In the present paper, details are given of the method of working, and it is suggested that on the addition of the halogen methyl ether to the magnesium alkyl haloid an additive compound, which may be represented by the following typical formula: $RR'BrO{\cdot}Mg{\cdot}OR''R'''Cl$, is formed in which the two oxygen atoms are quadrivalent, and is therefore analogous in constitution to the compound of ether and magnesium iodide studied by Zelinsky (Abstr., 1903, i, 802) and by Blaise (Abstr., 1905, i, 111).

T. A. H.

Relation of Tetramethylethylene Oxide to Pinacolin. Maurice Delacre (*Bull. Soc. chim.*, 1908, [iv], 3, 203—212).—It has been shown previously (Abstr., 1907, i, 581) that this oxide,  $O<\begin{matrix}CMe_2\\ |\\ CMe_2\end{matrix}$, may be best prepared from pinacone by Friedel's method, and in the present paper the purification of the oxide is described and its properties are given.

The oxide is not attacked by metallic sodium in presence of potassium hydroxide solution, and this method of freeing it from pinacolin, simultaneously produced, is used for its purification, the crude product obtained on reduction being fractionally distilled, and the fraction boiling at 91·6—91·8° under 743 mm. pressure being collected. It is a colourless liquid, with a piquant agreeable odour, has D 0 8311, is not attacked by its own volume of cold water, but is slowly hydrated in presence of a large excess of cold water, or more rapidly when heated with water in a closed vessel at 150°, or with water containing hydrochloric or sulphuric acid. The hydration is greatly retarded by the presence of an alkali hydroxide. The oxide gives with fuming hydrobromic acid a voluminous precipitate of a substance, which crystallises from light petroleum. The oxide is not reduced by sodium in presence of ether, or by sodium amalgam in alcohol.

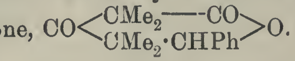
From a consideration of its properties, it is held that the direct isomerisation of the oxide to pinacolin in the absence of reagents is not likely to be realised, and it is pointed out that in its resistance to hydrogenation the oxide presents some analogy with α-benzopinacolin. T. A. H.

Chemistry of Lecithin. Paul Mayer (*Biochem. Zeitsch.*, 1908, 8, 199—202).—A reply to some criticisms of the author's work by I. Bang, in an article on the lipoid compounds (*Ergebnisse der Physiologie*, 1907, 6, 131). S. B. S.

Action of Metallic Magnesium on Certain Aliphatic Acids, and the Detection of Formic Acid. Henry J. H. Fenton and H. A. Sisson (*Proc. Camb. Phil. Soc.*, 1908, 14, 385. Compare Trans., 1907, 91, 687).—The reduction of acids by means of metallic magnesium only occurs in the lower members of a series, and has been observed in the case of formic, acetic, propionic, butyric, and oxalic acids.

As a specific test for formic acid, the solution to be examined is digested with magnesium ribbon or powder at the ordinary temperature for some minutes, and the resulting product is tested for formaldehyde by any of the usual colour tests. Soluble metallic formates give a similar result, but the reaction is much more delicate with the free acid. P. H.

Action of Magnesium on Esters of Brominated Fatty Acids. New Synthesis of β-Ketonic Esters. Josef Zeltner (*Ber.*, 1908, 41, 589—594).—The action of magnesium on an ethereal solution of brominated esters of the type $CHRBr\cdot CO_2Et$ (where R = Me, Et, or Pr) leads to the formation of the ester $CH_2R\cdot CO_2Et$ and of the β-ketonic ester, $CH_2R\cdot CO\cdot CHR\cdot CO_2Et$, the composition of which is determined by hydrolysis with 10% potassium hydroxide, whereby the dialkyl ketone, $CO(CH_2R)_2$, is obtained. Ethyl α-bromo*iso*butyrate reacts in a similar way, yielding ethyl α-*iso*butyryl*iso*butyrate. By the action of benzaldehyde on the ethereal solution of the product of interaction of magnesium and ethyl α-bromo*iso*butyrate, a *substance*, $C_{15}H_{18}O_3$, is obtained, m. p. 134—135°, which does not contain a carbonyl or hydroxyl group, yields benzaldehyde and di*iso*propyl ketone by hydrolysis with potassium hydroxide, and benzoic acid and the same ketone by oxidation with chromic acid; it is probably a δ-lactone,



$CO<\begin{matrix}CMe_2\text{——}CO\\CMe_2\cdot CHPh\end{matrix}>O$. C. S.

Electrolytic Reduction of Oleic to Stearic Acid. CHARLES MARIE (*Bull. Soc. chim.*, 1908, [iv], 3, 202—203).—It is stated that Fokin is wrong in assuming (Abstr., 1907, i, 10) that the author has expressed the opinion that in the electrolytic reduction of oleic to stearic acid the nature of the metallic cathode used has no influence on the reaction, since oleic acid was not included among the acids studied by him (Abstr., 1903, i, 605). The author's only contribution to this subject is a note (*Zeitsch. Elektrochem.*, 1905, 11, 649) in which it is merely stated that preliminary experiments on the reduction of oleic acid in alkaline solution gave yields as poor as those recorded by Petersen (Abstr., 1905, i, 678). T. A. H.

Action of Ozone on Compounds containing Triple Linkings. ETTORE MOLINARI (*Ber.*, 1908, **41**, 585—589. Compare Abstr., 1907, i, 1039).—In reply to Harries (this vol., i, 75), the author points out that the differences between the results of their work on the action of ozone on stearolic and phenylpropiolic acids are due to the fact that Harries uses ozonised oxygen, whilst he uses ozonised air.

He also claims priority in the study of the action of ozone on oils and their constituents. C. S.

Hydroxybehenic Acid. PH. EPIPHANOFF (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 133—138. Compare Fileti, Abstr., 1898, i, 236).—*β-Bromobehenic acid*, m. p. 32—33°, was obtained by treating brassic acid with hydrogen bromide in acetic acid solution. With potassium hydroxide, it yields *β-hydroxybehenic acid*,

$$C_8H_{17}\cdot CH(OH)\cdot CH_2\cdot C_{11}H_{22}\cdot CO_2H,$$

m. p. 89—91°, solidifying at 74—76°, and yielding a *monoacetyl* derivative, $C_{22}H_{43}O_3Ac$, with acetic anhydride. The *sodium*, *silver*, *calcium*, and *iodo*-derivatives have also been prepared. An attempt to obtain the β-hydroxy-acid by the action of sulphuric acid on erucic acid was unsuccessful. Z. K.

Synthesis of Dibasic Acids. III. GUSTAVE BLANC (*Bull. Soc. chim.*, 1908, [iv], 3, 286—292).—A continuation of work described in Abstr., 1905, i, 680, 681, giving a résumé of results already published in Abstr., 1905, i, 682; 1906, i, 399, 523; 1907, i, 763, 1058, and describing in somewhat greater detail the processes used in the preparation of the various dibasic acids and the intermediate products from the decomposition of which they result.

The following points have not been referred to previously: γ-*Bromo-αα-dimethylbutyric acid*, m. p. 48°, is obtained by adding water to the product of the action of phosphorus pentabromide on αα-dimethylbutyrolactone. When ethyl δ-bromo-ββ-dimethylvalerate, prepared as already described (Abstr., 1906, i, 399), is heated with potassium cyanide in presence of acetic acid and sodium iodide, ββ-dimethyladipic acid is obtained. T. A. H.

Synthesis of Dibasic Acids. IV. GUSTAVE BLANC (*Bull. Soc. chim.*, 1908, [iv], 3, 292—301).—A continuation of work already recorded (Abstr., 1905, i, 680, 681, and preceding abstract) and describing the preparation of β-*iso*propyladipic, ββ-dimethylpimelic, and ββε-trimethylpimelic acids by the general process already given (*loc. cit.*).

β-iso*Propylvalerolactone*, b. p. 138°/14 mm., obtained by the reduction of β-*iso*propylglutaric anhydride, for the preparation of which the method of Thorpe, Udall, and Howles (Trans., 1900, 77, 945) is preferred to that of Knoevenagel (Abstr., 1899, i, 116), is a colourless liquid with a lactonic odour, and is but slightly soluble in water or solutions of alkali carbonates; its *hydrazino*-derivative, m. p. 70°, prepared by Blaise and Luttringer's method (Abstr., 1905, i, 329), forms colourless scales. The lactone, on successive treatment with phosphorus pentabromide and alcohol, yields *ethyl δ-bromo-β*-iso*propylvalerate*, $CH_2Br \cdot CH_2 \cdot CHPr^{\beta} \cdot CH_2 \cdot CO_2Et$, b. p. 138°/14 mm., a colourless, mobile liquid of persistent odour. The conversion of this into *r-β-iso*propyladipic acid is accomplished in the same manner as that of ethyl δ-bromo-ββ-dimethylvalerate into dimethyladipic acid (see preceding abstract). *r-β-iso*Propyladipic acid crystallises readily from water containing formic acid, and melts at 85°, in place of 75—76° recorded by Wallach for β-*iso*propyladipic acid obtained by the oxidation of tetrahydrocarvone (Abstr., 1905, i, 451) and phellandrene (Abstr., 1906, i, 194). The remainder of the paper records results already published (Abstr., 1906, i, 399), but gives details of the experimental methods used. T. A. H.

Preparation of Adipic Acid from *cyclo*Hexanol. CARL MANNICH and V. H. HÂNCU (*Ber.*, 1908, 41, 575).—Adipic acid is conveniently prepared in quantity by the oxidation of *cyclo*hexanol in sodium carbonate solution with potassium permanganate at the ordinary temperature for three days, whereby 80 per cent. of the theoretical yield is obtained. E. F. A.

Digitoxonic Acid. HEINRICH KILIANI (*Ber.*, 1908, 41, 656. Compare Abstr., 1906, i, 66).—Neither digitoxonic acid nor its derivatives could be obtained previously in a crystalline form. A *phenylhydrazide*, $C_{12}H_{18}O_4N_2$, crystallising in needles, $[\alpha]_D -17{\cdot}1°$, by means of which the acid may be identified, has now been formed by treating the syrupy lactone, prepared by oxidation of digitoxose with bromine in aqueous solution (*loc. cit.*), with phenylhydrazine in alcoholic solution and adding dry ether after thirty-six hours.

G. Y.

Organic Iron Salts. Leopold Rosenthaler and A. Siebeck (*Arch. Pharm.*, 1908, **246**, 51—57. Compare Abstr., 1903, ii, 765).—The following have been prepared and analysed: *basic ferric tartrate*, $2[Fe_2(C_4H_4O_6)_3],3Fe(OH)_3,3H_2O$; *basic ferric citrate*,

$$6(FeC_6H_5O_7),7Fe(OH)_3,9H_2O;$$

basic ferric oxalate, $Fe_2(C_2O_4)_3,7Fe_2O_3,9H_2O$; *basic ferric malate*, $Fe_2(C_4H_4O_5)_3,2Fe(OH)_3,H_2O$. *Ferrous malate*, $Fe(C_4H_4O_5)$, and *normal ferric malate*, $Fe_2(C_4H_4O_5)_3$, could not be obtained pure. All these salts are amorphous precipitates; a separation of the acids cannot be effected by them.

G. B.

Saccharinic Acids. Heinrich Kiliani (*Ber.*, 1908, **41**, 469—470. Compare this vol., i, 128).—According to Nef's views on the formation of saccharinic acids (this vol., i, 5), lævulose should be one of the best materials from which to prepare *iso*saccharinic acid. This is now shown not to be the case, *iso*saccharinic acid being obtained, together with saccharinic acid, but only in a 1·7% yield on successive treatment of lævulose with calcium oxide and oxalic acid. *iso*Saccharinic acid is obtained in a similar yield from dextrose (probably directly and not from admixed maltose), but in a 15% yield from lactose.

G. Y.

Antimony Thioglycollate. Correction. Arthur Rosenheim (*Zeitsch. anorg. Chem.*, 1908, **57**, 359—360).—The statement by the author and Davidsohn (Abstr., 1904, i, 843) that a normal thioglycollate of antimony can be obtained by the action of antimony trichloride on thioglycollic acid is incorrect, the compound described having the formula given later by Klason and Carlson (Abstr., 1906, i, 232; compare Holmberg, this vol., ii, 130).

G. S.

Ketens. VI. Keten. Hermann Staudinger and Helmut W. Klever (*Ber.*, 1908, **41**, 594—600. Compare Abstr., 1907, i, 424; Wilsmore, Trans., 1907, **91**, 1939).—Pure keten, $CH_2{:}CO$, m. p. $-151°$, b. p. $-56°$, has been obtained by treating bromoacetyl bromide in ethyl acetate solution with zinc, rapidly distilling, and subsequently removing the keten from the warm solvent in a current of hydrogen, condensing it by liquid air, and removing traces of ethyl acetate by repeated fractionation at $-60°$. The purity was determined by estimating the ratio C/H. The keten is colourless in the solid, liquid, or gaseous states, and has an intolerable odour of chlorine and acetic anhydride. In ethereal solution, bromine converts it into bromoacetyl bromide, whilst dry oxygen has no action. Zinc chloride or ferric chloride causes the formation of dark-coloured polymerides; tertiary bases also induce polymerisation, dehydracetic acid being detected among the products. Keten does not form additive compounds with quinone, dibenzylideneacetone, or benzylideneaniline, or keten bases with pyridine or quinoline.

The striking difference between the reactions of keten and those of

disubstituted ketens lends weight to Wilsmore's suggestion that keten may be hydroxyacetylene, $CH⋮C{\cdot}OH$. When the pure keten, however, reacts with water, not a trace of an aldehyde can be detected, and an ethereal solution of keten does not react with potassium, sodium, or phenylcarbimide; the author considers therefore that a hydroxyl group is not present, and that keten has the formula $CH_2{:}CO$.
C. S.

Oxidation of Acetone by Potassium Permanganate. H. Fournier (*Bull. Soc. chim.*, 1908, [iv], 3, 259—265).—In addition to acetic, oxalic, and carbonic acids, which previous workers have obtained by the action of potassium permanganate on acetone, the author has obtained pyruvic acid, and has investigated the influence of various factors on the yield of this acid.

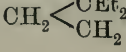
The acid was isolated and weighed in the form of the phenyhydrazone. The four acids mentioned are always produced when acetone is oxidised in presence of alkali with sufficient permanganate to furnish less than 5 atoms of oxygen per mol. of the ketone and at temperatures between $-2°$ and 25°. Pyruvic acid is formed only in small amount, and the quantity produced is greatly influenced by the amount of the oxidising agent used, the concentration of the alkali and the ketone, the temperature at which the reaction is conducted, and the time taken to effect the oxidation.

The oxidation of acetone by permanganate in neutral solution is slow, and is greatly accelerated by the addition of sodium, calcium, or barium hydroxide, or normal carbonates of the alkalis. T. A. H.

Reactions of β-Chloroethyl- and Vinyl-ketones. M. Maire (*Bull. Soc. chim.*, 1908, [iv], 3, 280—286).—In continuation of previous work on these ketones (see Abstr., 1907, i, 241, 418; this vol., i, 290), an account is given of the products obtained (1) by their fixation of hydrogen cyanide, halogens, and haloid acids, and (2) by their interaction with organo-magnesium haloids.

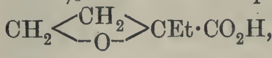
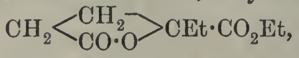
β-Bromoethyl ethyl ketone, $CH_2Br{\cdot}CH_2{\cdot}COEt$, b. p. 72°/16 mm., obtained by the action of hydrogen bromide on ethyl vinyl ketone, is a liquid, which is at first colourless, but rapidly darkens to almost black; the *semicarbazone* is colourless and crystalline.

aβ-Dibromoethyl ethyl ketone, b. p. 97°/13 mm., similarly obtained by the addition of bromine to ethyl vinyl ketone, is a heavy liquid of sharp odour. Ethyl vinyl ketone, on treatment with a drop of sulphuric acid in presence of ethyl orthoformate, yields the corresponding *diethylacetal*, $CEt(OEt)_2{\cdot}CH{:}CH_2$, b. p. 76—78°/15 mm., a pleasant-smelling liquid.

β-Chloroethyl ethyl ketone reacts with magnesium ethyl bromide in ether to form *diethyl-β-chloroethylcarbinol*, $CH_2Cl{\cdot}CH_2{\cdot}CEt_2{\cdot}OH$, b. p. 90°/13 mm., a liquid with a slightly camphoraceous odour. Attempts to prepare a phenylurethane and an acetyl derivative resulted in dehydration of the chloro-alcohol. When warmed with a 50% solution of potassium hydroxide, the chloro-alcohol furnished the *oxide*,  $CH_2{<}\begin{matrix}CEt_2\\CH_2\end{matrix}{>}O$, b. p. 126°, a liquid with a penetrating camphoraceous odour. On treatment with diethylamine, the chloro-alcohol yields the corresponding *β-diethylamino*-derivative,

$$NEt_2\cdot CH_2\cdot CH_2\cdot CEt_2\cdot OH,$$

b. p. 93—95°/7 mm., a liquid with a slightly basic odour. No benzoyl derivative of this amino-alcohol could be obtained.

β-Chloroethyl ethyl ketone, on treatment with 1 mol. of potassium cyanide and the equivalent quantity of sulphuric acid and hydrolysis of the resulting nitrile with hydrochloric acid, furnishes *ethyl γ-chloro-α-hydroxy-α-ethylbutyrate*, $CH_2Cl\cdot CH_2\cdot CEt(OH)\cdot CO_2Et$, b. p. 112°/15 mm., an almost inodorous liquid, which on treatment with a 50% solution of potassium hydroxide gives the *acid αγ-oxide*,  $CH_2<\begin{matrix}CH_2\\ -O-\end{matrix}>CEt\cdot CO_2H$, b. p. 136°/16 mm., a viscous, inodorous liquid, which is much more stable than the corresponding αβ-acid oxide. Ethyl vinyl ketone, on treatment with 1 mol. of potassium cyanide in presence of ½ mol. of sulphuric acid and hydrolysis of the resulting nitrile with hydrochloric acid and subsequent esterification, yields *ethyl β-propionylpropionate*, $COEt\cdot CH_2\cdot CH_2\cdot CO_2Et$, b. p. 106°/16 mm., a colourless liquid with a feeble odour; the *semicarbazone*, m. p. 106°, crystallises from ethyl acetate on adding light petroleum. The free acid, m. p. 36—37°, forms long tablets from ether and light petroleum, is hygroscopic, and is not coloured red by ferric chloride (compare Zanetti, Abstr., 1892, 351). On treatment with 1 mol. of hydrogen cyanide and subsequent hydrolysis and esterification, it yields *ethyl γ-ethylbutyrolactone-γ-carboxylate*,  $CH_2<\begin{matrix}CH_2-\\ CO\cdot O\end{matrix}>CEt\cdot CO_2Et$, b. p. 156°/16 mm., which may also be obtained directly from ethyl vinyl ketone by the addition of 2 mols. of hydrocyanic acid. The free *lactonic acid*, obtained by hydrolysing the ethyl ester, is a viscous liquid, b. p. 204°/16 mm. T. A. H.

Syntheses by means of the Mixed Organometallic Derivatives of Zinc. Ketone-alcohols. Edmond E. Blaise and I. Hermann (*Compt. rend.*, 1908, **146**, 479—481).—It has been shown previously (Abstr., 1907, i, 750; this vol., i, 78) that β-acetoxy-acid chlorides interact with the mixed organometallic derivatives of zinc to form the corresponding β-acetoxy-ketones, and, in the case when the α-carbon atom is associated with hydrogen, hydrolysis of the acetoxy-ketone does not yield the hydroxy-ketone, but the corresponding unsaturated ketone. In the present paper, it is shown that αα-disubstituted β-hydroxy-ketones can be prepared by hydrolysis of the corresponding acetoxy-derivative. Hydroxypivalyl chloride (β-hydroxy-αα-dimethylpropionyl chloride), prepared by the action of thionyl chloride on the acid, is converted by the action of zinc ethyl iodide to the extent of 80% into *ethyl acetoxy* tert.*-butyl ketone*,

$$OAc\cdot CH_2\cdot CMe_2\cdot COEt,$$

m. p. 27°, b. p. 98—99°/14 mm. *Ethyl hydroxy*tert.*-butyl ketone*, $OH\cdot CH_2\cdot CMe_2\cdot COEt$, obtained by hydrolysing the acetyl derivative with cold sodium hydroxide solution, is a liquid, b. p. 88°/8 mm., and yields a phenylurethane, oxime, semicarbazone, and p-nitrophenylhydrazone.

When ethyl acetoxy*tert.*-butyl ketone is boiled with 10% aqueous potassium hydroxide, it yields formic acid, formaldehyde, and a mixture of ketones, from which ethyl *iso*propyl ketone has been isolated, and an unsaturated C_7 ketone, which probably has the constitution represented by the formula $CMe_2{\cdot}CO{\cdot}CMe{:}CH_2$. M. A. W.

Preparation and Properties of Crystallised *d*-Talitol. Gabriel Bertrand and P. Bruneau (*Compt. rend.*, 1908, **146**, 482—484).—Crystallised *d*-talitol can be obtained to the extent of 7·5% from *d*-galactonic acid by means of the following series of reactions: *d*-galactonic acid is partly converted into *d*-talonic acid by heating with pyridine for three hours at 130°, from the mixed calcium salts of the two acids the less soluble galactonate is separated by fractional crystallisation, and the talonic acid is liberated from the mother liquor by means of oxalic acid and converted into the lactone by distillation in a vacuum and subsequent heating for five hours on a water-bath. The lactone is reduced by means of sodium amalgam at 0° to talose, and this on further reduction at 10—20° in a neutral or slightly alkaline medium is converted into talitol, which is isolated in the form of its tribenzylidene derivative (Bertrand and Lanzenberg, Abstr., 1906, i, 728). The *d*-talitol, obtained in the form of a syrup from the tribenzylidene derivative, is crystallised from absolute alcohol; it forms compact, crystalline nodules, m. p. 86°, on the Maquenne metallic block, and has $[\alpha]_D$ +3·05° in 10% aqueous solution at 18°. The tribenzylidene derivative has m. p. 206° on the Maquenne metallic block [Fischer gives 210° (corr.), Abstr., 1894, i, 395]. M. A. W.

The Properties of Pure Starch. Léon Maquenne (*Compt. rend.*, 1908, **146**, 317—318).—The starch deposited, in a granular form resembling natural starch grains, from Fouard's perfect starch solution (this vol., i, 138) is identical with the amylose described by Maquenne and Roux (Abstr., 1905, i, 511, and there termed amylocellulose; a name since changed by them to amylose). Its resemblance to natural starch has led these authors to the conclusion that starch consists of a perfect solution of amylose thickened by amylopectin. The opalescence and precipitation observed by Fouard is the phenomenon called "retrogradation" by Maquenne and Roux, who suggested that it is due either to pseudo-crystallisation or to a polymerisation similar to those undergone by certain sugars, dihydroxyacetone, &c. In view of the variation in the rotatory power of amylose solution with dilution (Fouard), the second of these two theories becomes more probable. Moreover, the phenomenon is reversible, the precipitate dissolving in water under pressure. E. H.

Nature of Iodide of Starch. Maurice Padoa (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 214—215).—A criticism of Katayama's results (compare this vol., i, 9).—It is pointed out that the colorimetric methods of measurement employed by that author give results of doubtful value, since, when such methods are applied to suspensions, the size of the particles may influence both the quality and the quantity of the coloration. Further, conclusions drawn from the coefficient of distribution of iodine between solutions of iodide of starch and carbon tetrachloride would be valid only if the phase law were applicable, which is not the case ; there is no authority for considering a suspension either as a single phase or as composed of two phases, neither can it be admitted that amorphous compounds or substances in the form of minute, suspended particles are capable of forming solutions which are saturated in the sense in which this term is applied to solutions of crystalline substances (compare also Padoa and Savarè, Abstr., 1905, i, 416 ; Skrabal, Abstr., 1907, ii, 448). T. H. P.

Cellulose and its Derivatives. Eugène Grandmougin (*Chem. Zeit.*, 1908, **32**, 241—242).—A summary of recently published work on the constitution of cellulose and its derivatives. P. H.

Humus Substances Soluble in Water from Scandinavian Fresh Waters. Ossian Aschan (*J. pr. Chem.*, 1908, [ii], **77**, 172—188).—A study of the amount and nature of the dissolved humus substances in the lake and river waters of Finland. These waters are all coloured yellow to brown. The solutions of such humus substances are probably colloidal, and are termed *hummussoles*, an abbreviation of humus hydrosols. The original must be consulted for the method of isolation of these substances, and for the analytical details. The analytical results quoted by previous authors were obtained with substances dried at high temperatures, and are therefore not to be depended on. The results now given approach the percentage composition of the polysaccharides ; small amounts of nitrogen are present in the form of protein substances ; sulphur is found mostly in traces. Although the formation of humates, the decomposition of the insoluble humates by alkalis, and the liberation of the humus substances, on addition of an acid to their concentrated alkaline solutions, as a flocculent precipitate soluble in alkalis, indicate that the humus substances are acid in nature, yet their acidity is scarcely greater than that of phenol, and it remains possible that the so-called humates are not salts, but colloidal combinations of varying composition. These views are illustrated by a number of experiments on the formation and decomposition of the ferric humates, the precipitation of the hummussoles by other metallic salts, and the action of electrolytes on the solutions of the ferric humates. G. Y.

Preparation of Amino-alcohols. J. D. Riedel (D.R.-P. 189481. Compare Abstr., 1906, i, 631).—When the halogen hydrins having the general formula $OH\cdot CRR'\cdot CH_2Cl$(Br or I) are heated at 125° for about a day with aqueous or alcoholic ammonia, they are converted into a mixture of primary and secondary amines having the general formulæ $NH_2\cdot CH_2\cdot CRR'\cdot OH$ and $NH(CH_2\cdot CRR'\cdot OH)_2$. The acyl and other derivatives of these bases have valuable therapeutic properties.

Chlorohydrin gives rise to *aminodimethylethylcarbinol*,

$$NH_2\cdot CH_2\cdot CMeEt\cdot OH,$$

a viscid base, miscible with water, b. p. 75—80°/30 mm. ; crystalline, hygroscopic *hydrochloride,* soluble in acetone; *divaleryl* derivative, b. p. 190°/32 mm., m. p. 50°; *dibromovaleryl* derivative, needles from light petroleum, m. p. 74°. *Iminobisdimethylethylcarbinol,* a by-product in the foregoing reaction, is very viscid and insoluble in water; its *hydrochloride,* m. p. 144°, crystallises from acetone in nacreous leaflets. Chlorodimethyl*iso*amylcarbinol gives rise to *aminodimethyl*iso*amylcarbinol,* $NH_2{\cdot}CH_2{\cdot}CMe(C_5H_{11}){\cdot}OH$, b. p. 125°/68 mm., and *iminobisdimethyl*iso*amylcarbinol,* a solid base, b. p. 206—207°/46 mm. Phenylchlorodimethylcarbinol, $CH_2Cl{\cdot}CMePh{\cdot}OH$, furnishes *aminophenyldimethylcarbinol,* $NH_2{\cdot}CH_2{\cdot}CMePh{\cdot}OH$, b. p. 175°/40 mm., and *iminobisaminophenyldimethylcarbinol,* $NH(CH_2{\cdot}CMePh{\cdot}OH)_2$, b. p. 258°/40 mm.; *hydrochloride,* m. p. 228—229°. G. T. M.

Synthesis of Imino- and Nitrilo-Acids. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 140—141. Compare Abstr., 1907, i, 1015, 1016).—The explanation previously given of the mode of formation of iminodicarboxylic acids is amplified further. The reaction between an amino-nitrile or an ester of an amino-acid and a hydroxy-nitrile proceeds in two phases, thus: I. $CN{\cdot}R{\cdot}CH{\cdot}NH_2 + OH{\cdot}CH(CN){\cdot}R = NH(CHR{\cdot}CN)_2{<}^{H}_{OH} \longrightarrow$ II. $NH(CHR{\cdot}CN)_2 + H_2O$. The formation of nitrilopropionitrile by Passavant (Abstr., 1880, ii, 313) is explained similarly; thus $NH(CHMe{\cdot}CN)_2 + CHMe{<}^{OH}_{CN} \longrightarrow NH(CHMe{\cdot}CN)_3{\cdot}OH \longrightarrow N(CHMe{\cdot}CN)_3 + H_2O$. If, on the other hand, there were a heavy radicle in the imino-derivative, the intermediate product would decompose, forming a hydroxy-acid and an imino-nitrile of lower molecular weight. Z. K.

Action of Mercury Diethyl on Mercury Fulminate; Decomposition of the Mixture by Hydrochloric Acid. New Complex, $5HgCl_2,2NH_2{\cdot}OH,HCl,2NH_4Cl,2Me_2CO$. PAVEL GRIGOROWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1113—1119).—Previous theories regarding the constitution of mercury fulminate are examined, and its reaction with organometallic compounds has been investigated. On mixing perfectly dry mercury diethyl with mercury fulminate, there is no apparent reaction, but, when hydrogen chloride is passed in continuously for three days, the appearance of the mixture changes, and benzene extracts mercury ethyl chloride. The residue extracted with acetone yields the *compound*

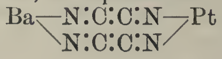
$$5HgCl_2,2NH_2{\cdot}OH,HCl,2NH_4Cl,2COMe_2,$$

which commences to melt at 50°, and at 100° loses acetone, forming $5HgCl_2,2NH_2{\cdot}OH,HCl,2NH_4Cl$, m. p. above 300° (decomp.). The acetone compound can also be formed by dissolving mercuric chloride, ammonium chloride, and hydroxylamine hydrochloride in the necessary proportions in acetone, and allowing the excess of the latter to evaporate. Since additive products of mercury diethyl and mercury fulminate are not formed, it is highly improbable that the carbon in the latter is bivalent, and its formula is most probably $N{<}^{CH}_{O}$ (with a bond from CH to O), or $H{\cdot}C{\vdots}N{:}O$. Z. K.

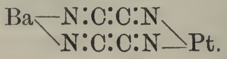
Preparation of Derivatives of Cyanogen Bromide and of Cyanamide. FRITZ BAUM (*Ber.*, 1908, **41**, 523—524).—A modification of Scholl's method (Abstr., 1896, i, 585) for the preparation of cyanogen bromide is recommended in those cases where the reagent need not be isolated. A somewhat dilute cold solution of potassium cyanide is dropped slowly into well-cooled bromine covered with water, and the resulting crystalline paste extracted with ether. The ethereal solution is dried over calcium chloride, made up to a definite volume, and the amount of cyanogen bromide calculated from the original quantity of bromine, or estimated by titration with sodium ethoxide.

The ethereal solution of cyanogen bromide reacts with methylamine or aniline to form methylcyanamide or phenylcyanamide, which readily polymerise to termolecular forms, and must therefore be used at once in the preparation of ethyl cyanoanilinoacetate and of cyanoacetylmethylcarbamide (below). C. S.

Platinocyanides. LEONARD A. LEVY (*Proc. Camb. Phil. Soc.*, 1908, **14**, 378—380. Compare Abstr., 1907, i, 689).—When barium platinocyanide crystallises from solutions containing hydroxyl ions, it separates in green, markedly fluorescent crystals, whereas from slightly acid solutions it separates in yellow crystals which fluoresce but slightly. The difference in these two forms is attributed to stereoisomerism, as represented by the two formulæ:



and



P. H.

Formation of a Double Compound of Mercuric Cyanide and Pyridine. JOHANNES SCHROEDER (*J. pr. Chem.*, 1908, [ii], **77**, 269—270).—In continuation of the study of pyridine as a solvent for metallic salts (Abstr., 1905, ii, 306), mercuric cyanide is now found to form a double *compound* with pyridine, $Hg(CN)_2,2C_5H_5N$, which is obtained in colourless crystals. The compound is decomposed by water, as the molecular weight determination in aqueous solution gives results approximately one-third of that corresponding with the double compound. G. Y.

Organic Salts of Carbamide and Acylcarbamides. FRITZ BAUM (*Ber.*, 1908, **41**, 525—532).—Experiments carried out with the object of preparing asymmetrical cyanoacetylmethylcarbamide lead to a study of the interaction of cyanoacetic acid and methylcyanamide. These compounds react very energetically, and, if ether is used as diluent, Traube's symmetrical cyanoacetylmethylcarbamide is obtained in 50% yield (Abstr., 1901, i, 54); the remaining product is soluble in water, and ultimately became crystalline and proved to be *methyl carbamide cyanoacetate*. Cyanamide and cyanoacetic acid yield carbamide cyanoacetate in aqueous solution; on further keeping, heat is developed, and cyanoacetylcarbamide and carbamide can be isolated afterwards. The action of the acid on the cyanamide is therefore, in the first instance, hydration of the cyanamide to carbamide, next formation of the salt, and then dehydration, yielding substituted carbamides.

This theory of the reaction was proved as follows: (1) it is already known that cyanamide can be hydrated by 50% mineral acid; (2) the formation of salts by melting carbamide and acid together. In this way, it is shown that acetic acid forms no salts with carbamide, methyl-, dimethyl-, or phenyl-carbamides; chloroacetic acid forms salts with methyl- (m. p. 27·5—30°) and dimethyl-carbamides, containing 1 mol. of carbamide and 2 mols. of acid, but not with carbamide itself or phenylcarbamide. Cyanoacetic acid forms salts with all these carbamides. The crude salt containing one of carbamide to one of acid has m. p. 71—74°, that containing 2 mols. of acid forms stout crystals, m. p. 94—95°, and this can also be obtained from cyanamide. With methyl carbamide, 1 : 1, m. p. 41—41·5°, with 2 mols. of acid the product is oily, as is also the case with dimethylcarbamide, both with 1 or 2 mols. of acid.

These salts may be dehydrated by acetic anhydride, which is better than phosphorus pentachloride (Mulder, Abstr., 1879, 618) or phosphoryl chloride (Traube, *loc. cit.*). In this way, the straight-chain *cyanoacetyldimethylcarbamide*, $C_6H_9O_2N_3$, was prepared, forming monoclinic prisms, m. p. 77·5—78·5° (compare Farbenfabriken vorm. Friedr. Bayer & Co., Abstr., 1906, i, 634; 1907, i, 195). W. R.

Picrolonates. VII. Guanidines. Henry L. Wheeler and George S. Jamieson (*J. Biol. Chem.*, 1908, 4, 111—117).—The picrolonates of the following have been prepared and analysed: cytosine, $C_4H_5ON_3,C_{10}H_8O_5N_4$, m. p. 270—273°; 2-amino-6-oxypyrimidine (*iso*cytosine), $C_4H_5ON_3,C_{10}H_8O_5N_4$, m. p. 273—275°; 6-aminopyrimidine, $C_4H_5N_3,C_{10}H_8O_5N_4$, m. p. 261°; 6-oxypyrimidine, $C_4H_4ON_2,C_{10}H_8O_5N_4$, m. p. 191—193°; 1-methylguanidine,

$$C_2H_7N_3,C_{10}H_8O_5N_4,$$

m. p. 291°; ββ-dimethylguanidine, $C_3H_9N_3,C_{10}H_8O_5N_4$, m. p. 278°; αβ-dimethylguanidine, m. p. 262°; β-ethyl-ψ-thiocarbamide,

$$C_3H_8N_2S,C_{10}H_8O_5N_4,$$

m. p. 225°. The picrates of the three bases last-named melted at 224°, 178°, and 187° respectively.

The method employed in the synthesis of the substituted guanidines was to leave the methyl iodide additive product of the thiocarbamide at the ordinary temperature with a concentrated aqueous solution of methyl- or dimethyl-amine. G. B.

Ethyl Malonylbishydrazoneacetoacetate, a Substance with Three Reactive Methylene Groups. Carl Bülow (*Ber.*, 1908, 41, 641—646. Compare Abstr., 1905, i, 660; 1907, i, 301, 986; Curtius, Schöfer, and Schwan, Abstr., 1895, i, 263).—As ethyl malonylbishydrazoneacetoacetate,

$$CH_2(CO\cdot NH\cdot N\colon CMe\cdot CH_2\cdot CO_2Et)_2,$$

contains three reactive methylene and two imino-groups, it must form the starting point for the preparation of a large number of compounds, the formation and reactions of which may be expected to throw light on the nature of such substances in general. An account is now given of the results of the study of the action of diazo-compounds on the bishydrazone ester.

Ethyl malonylbishydrazoneacetoacetate, $C_{15}H_{24}O_6N_4$, prepared by the action of malonyldihydrazide (Bülow and Weidlich, Abstr., 1906, i, 981) on ethyl acetoacetate at 30°, crystallises from a mixture of chloroform and light petroleum in needles, m. p. 96—96·5°, decomp. 147—150°, forming a yellow *oil*, and, when dissolved in water, gradually deposits a white, crystalline *derivative*, m. p. 147°, decomposing to a *substance*, m. p. 243—244°. When treated with diazobenzene chloride in aqueous-alcoholic sodium acetate solution at 10°, ethyl malonylbishydrazoneacetoacetate forms *ethyl phenylhydrazonemesoxalylbishydrazonebenzeneazoacetoacetate*,

$$NHPh\cdot N\colon C[CO\cdot NH\cdot N\colon CMe\cdot CH(N_2Ph)\cdot CO_2Et]_2,$$

which, when recrystallised rapidly from glacial acetic acid, separates in needles, m. p. 222·5°, is sparingly soluble in alcohol, and on prolonged boiling with acetic acid is converted into two *substances*, one sparingly, the other readily, soluble in alcohol. G. Y.

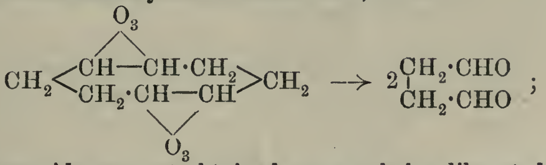
Reciprocal Transformations of Magnesium Ammonium and Magnesium Oxonium Compounds. WLADIMIR TSCHELINZEFF (*Ber.*, 1908, **41**, 646—655. Compare Abstr., 1907, i, 499).—A study of the action of amines on organo-magnesium ethers, and of ethers on organo-magnesium amine complexes. Organo-magnesium compounds form complexes with 1 mol., $MgRX,R_2'O$, and with 2 mols.,

$$MgRX,2R_2'O,$$

of ethers, but with only 1 mol. of an amine, $MgRX,NR_3'$; these last, although not capable of forming additive compounds with amines, form with ethers the complexes, $MgRX,NR_3',R_2''O$. It is argued that there must exist in the organo-magnesium molecule two unsaturated positions, and that, whilst an ether molecule can be added on to each of these positions, an amine molecule can be added on to only one.

The displacement of an ether by an amine molecule, or conversely of an amine by an ether molecule, is determined more by the nature of the groups in these molecules than by the fact of the one being an oxygen and the other a nitrogen compound. In the action of ethers on ether complexes, or of amines on amine complexes, the compound formed is that having the greater heat of formation; the action may lead to the formation of mixtures. The action of ethers on organo-magnesium ammonium compounds is at first additive, and with aliphatic amines ends at the formation of the amine-ether complex, but with aromatic amines proceeds to the formation of diether complexes. The action of an amine on a monoether complex must be substitutive, but the displaced ether molecule is added on to the second unsaturated position in the organo-magnesium compound, the product of the whole reaction being an amine-ether complex. G. Y.

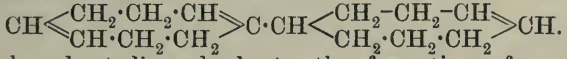
Constitution of *cyclo*Octadiene from ψ-Pelletierine. CARL D. HARRIES (*Ber.*, 1908, **41**, 671—678).—Willstätter and Veraguth's *cyclo*octadiene, obtained by the distillation of *des*-dimethylgranatanine methyl hydroxide (Abstr., 1905, i, 515, 543), was considered by these authors to have conjugated double linkings from its readiness in polymerising (Abstr., 1907, i, 303). The conclusion has been drawn that caoutchouc is a polymeride of dimethyl*cyclo*octa-$\Delta^{1:5}$-diene (Abstr., 1905, i, 364), and the great similarity between these substances suggested that the hydrocarbon from ψ-pelletierine had also its double linkings in positions 1 and 5. A study of the action of ozone on the hydrocarbon has proved it to consist of 80% of *cyclo*octa-$\Delta^{1:5}$-diene, because the diozonide is decomposed by heating with water for two hours into succindialdehyde or succinic acid, thus :



hydrogen peroxide was not obtained, oxygen being liberated.

cyclo*Octa-$\Delta^{1:5}$-diene diozonide* separates from a carbon tetrachloride solution as a white, amorphous, sparingly soluble mass on treatment for eight hours with ozone diluted with carbon dioxide. After removal of the carbon tetrachloride by distillation in a vacuum, the mother liquor deposits impure cyclo*octadiene monozonide*, $C_8H_{12}O_3$, as a syrup.

Di*cyclo*octadiene (*loc. cit.*, 1905, 515) yields an explosive ozonide, which on treatment with water gives succindialdehyde, and analysis shows it to be a mixture of the diozonide described and a *triozonide*, $C_{16}H_{24}O_9$; from this result, the deduction is made that the constitution of the hydrocarbon is :



$$CH{\lessgtr}\begin{matrix}CH_2{\cdot}CH_2{\cdot}CH\\CH{\cdot}CH_2{\cdot}CH_2\end{matrix}{\gtrless}C{\cdot}CH{<}\begin{matrix}CH_2{-}CH_2{-}CH\\CH_2{\cdot}CH_2{\cdot}CH_2\end{matrix}{\gtrless}CH.$$

The poly*cyclo*octadiene leads to the formation of a product of composition intermediate between $C_8H_{12}O_3$ and $C_{16}H_{24}O_9$. There is therefore no direct connexion between this and gutta-percha (Abstr., 1906, i, 30).

A series of experiments on the polymerisation of *cyclo*octadiene were carried out to ascertain whether it was possible to convert it into caoutchouc or gutta-percha like products. Spontaneous polymerisation on slowly warming to 60°, or in the cold, or with boron trifluoride in the hot, lead to Willstätter's polymerides, but boron trifluoride, hydrogen chloride, or phosphoric oxide in the cold lead to the formation of another *polymeride*, m. p. 115—120°, in addition to the two previously known, the ozonide of which forms succindialdehyde with water. W. R.

Equilibrium of Hydrogenation. MAURICE PADOA and UGO FABRIS (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 111—115).—The authors have studied the reversibility or otherwise of the hydrogenation of various hydrocarbons in presence of metallic catalysts.

Anthracene, when treated with hydrogen in presence of reduced nickel at 300—330°, yields tetrahydroanthracene (compare Godchot, Abstr., 1904, i, 987) and a small proportion of a product which smells strongly of naphthalene and no longer contains the anthracene nucleus. So that, in this case, there is no question of an equilibrium between the anthracene and the products of hydrogenation.

At 200°, naphthalene is hydrogenated to tetrahydronaphthalene, whilst at 300° the latter, in presence of hydrogen and reduced nickel, is converted into naphthalene, which itself undergoes no hydrogenation at this temperature. The reaction is hence, in this case, reversible.

Indene undergoes no hydrogenation at 300°, but is converted into hydrindene at 200°. When heated at 300° in presence of hydrogen and reduced nickel, hydrindene is partly decomposed into indene and hydrogen and partly destroyed.

At 300°, acenaphthene undergoes hydrogenation to tetrahydroacenaphthene, and the latter, when heated at 300° in presence of reduced nickel, is partly destroyed and partly converted into acenaphthene. When the vapour of acenaphthene is passed over lead oxide at a dull red heat, dehydroacenaphthene is formed, but this reaction does not take place in presence of reduced nickel at temperatures between 300° and 500°. When dehydroacenaphthene is hydrogenated at 250°, it yields tetrahydroacenaphthene. T. H. P.

Simultaneous Production of 1 : 6- and 2 : 7-Dimethylanthracenes in the Action of Methylene Dichloride, Chloroform, or Acetylene Tetrabromide on Toluene in the Presence of Aluminium Chloride. James Lavaux (*Compt. rend.*, 1908, **146**, 345—347).—It has been stated previously that in seven out of fifteen cases of the formation of dimethylanthracene, the product consists of the mixture of the 1 : 6 and 2 : 7 isomerides (this vol., i, 150). In the cases of the action of methylene chloride (Friedel and Crafts, Abstr., 1887, 1102), of chloroform (Elbs and Wittich, Abstr., 1885, 517), and of acetylene tetrabromide (Anschütz and Römig, Abstr., 1885, 768) on toluene in the presence of aluminium chloride, the author offers the following explanation of the sole production of the above two isomerides. In the first place, ditolylmethane, ditolylchloromethane, and ditolyldibromoethane are formed, and it has been shown for the first compound, and deduced by analogy for the others, that the product consists of a mixture almost solely composed of the symmetrical derivatives. Secondly, the latter, reacting with a second molecule of methylene dichloride or chloroform, or losing 2HBr, can only give 1 : 6-, 1 : 8-, or 2 : 7-dimethylanthracene derivatives, of which the 1 : 8 isomeride is formed in relatively small quantities. Lastly, the dihydro- and dichloro-derivatives formed in the first two reactions lose hydrogen and chlorine respectively by reaction with excess of methylene chloride and chloroform, giving the dimethylanthracenes themselves. E. H.

Orientation of a Series of Substituted Bromoanilines. John R. Hill (*Proc. Camb. Phil. Soc.*, 1908, **14**, 351—353. Compare Abstr., 1907, i, 692).—The bromine atom in each of the five compounds, methylethyl-, methyl-*n*-propyl-, methyl*iso*propyl-, methyl*iso*butyl-, and methyl*iso*amyl-bromoanilines, described previously (*loc. cit.*) was proved to be in the para-position by converting them into their corresponding *methiodides*, melting at 189°, 170°, 167°, 167°, and 176° respectively. These substances when heated in sealed tubes at 100° with a large excess of methyl iodide all yielded the same *p*-bromophenyltrimethylammonium iodide, m. p. 200°, which was itself synthesised from *p*-bromodimethylaniline and methyl iodide. P. H.

Resolution of Optically Active Ammonium Salts by means of Tartaric Acid. HUMPHREY O. JONES (*Proc. Camb. Phil. Soc.*, 1908, **14**, 376—377).—Previous attempts by the author to effect the resolution of phenylbenzylmethylethylammonium salts by means of camphorsulphonic acids (Jones, Trans., 1903, **83**, 1419; 1904, **85**, 223) having been only partly successful, the acid *d*-tartrate of the ammonium hydroxide was prepared; this substance on recrystallisation from rectified spirit yielded a lævorotatory *salt*,

$$C_7H_7\cdot NMeEtPh\cdot C_4H_5O_6,2H_2O,$$

m. p. 90—93°, $[M]_D$ −240°. Taking the value $[M]_D$ +42° for the acid tartrate ion, the value for the basic ion becomes $[M]_D$ −282°. The results cannot yet be regarded as final. P. H.

Isomerism of Disulphides. OSCAR HINSBERG (*Ber.*, 1908, **41**, 626—634. Compare Abstr., 1906, i, 654).—A third modification of 4:4′-dithioacetanilide, namely, γ-dithioacetanilide, is obtained when an acetic acid solution of the β-modification is exposed to sunlight for twelve days. It appears to be stereoisomeric with the β-compound, from which it is most readily separated by extraction with ethyl alcohol at 0°, in which the β-compound is almost insoluble. It is purified by precipitation with water and crystallisation from a mixture of methyl alcohol and water, when it is obtained in the form of crystalline crusts containing $1H_2O$ and melting at 120—122°. The same compound may be obtained together with the β-compound by oxidising *p*-acetylaminothiophenol with ferric chloride, and, when reduced, yields acetylaminophenylmercaptan. When hydrolysed with dilute sulphuric acid, it yields a dithioaniline in the form of a yellow powder, different from the ordinary *pp*-dithioaniline (m. p. 76—77°).

A second product, formed on exposure of β-dithioacetanilide to sunlight, is *ψ-dithioacetanilide*, $C_{12}H_{10}N_2S_2Ac_2$, which can be purified by crystallisation from alcohol and glacial acetic acid. It forms slender needles, m. p. 162°, containing acetic acid of crystallisation, or m. p. 160° containing alcohol of crystallisation. When reduced with aluminium powder, acetic and hydrochloric acids, it yields a sparingly soluble mercaptan, which dissolves in dilute sodium hydroxide solution. When hydrolysed, the ψ-compound yields a yellow-coloured base, which can be transformed into a colourless, crystalline sulphate.

Benzyl disulphide, when exposed to sunlight in acetic acid solution in the presence of iodine for several days, yields an isomeride, β-benzyl disulphide, m. p. 69—70°, which is more readily soluble in alcohol or glacial acetic acid than the original α-disulphide. When reduced, it yields benzyl mercaptan; when warmed with alcohol and sodium hydroxide solution, it is converted into the original α-compound. A mixture of the α- and β-compounds crystallises with $1CH_3\cdot OH$.

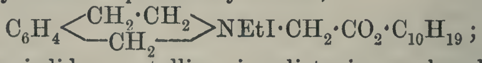
J. J. S.

Asymmetric Nitrogen. XXXI. Stereoisomerism Resulting from the Combination of Asymmetric Nitrogen with Asymmetric Carbon and the Problem of the Asymmetric Synthesis of Ammonium Bases. Edgar Wedekind and O. Wedekind (*Ber.*, 1908, **41**, 456—463).—Although the problem of the asymmetric synthesis of carbon compounds has been to some extent solved by the work of Marckwald (Abstr., 1904, i, 221, 470) and of McKenzie (Trans., 1905, **87**, 1373), an asymmetric synthesis in the simplest manner, the formation of an active form in an active solvent, has not yet been accomplished. An asymmetric synthesis in this manner has now been attempted, but without success, in the nitrogen series. Phenylbenzylmethylallylammonium iodide has been prepared by the action of allyl iodide on benzylmethylaniline in various optically active solvents, such as *d*-limonene, *l*-menthol, and *l*-menthyl chloromethyl ether, and under varying conditions as to concentration and fractional formation of the salt, but an optically active salt has not been obtained in any case. On the other hand, mixtures of optically active salts, which can be separated more or less completely by recrystallisation, are obtained by the action of *l*-menthyl iodoacetate on *N*-ethyltetrahydro*iso*quinoline and on methyl*iso*butylbenzylamine. More feeble bases enter into reaction with the *l*-menthyl ester only with great difficulty, if at all, whilst stronger bases liberate hydrogen iodide from the iodo-ester and form hydriodides.

l-*Menthyl iodoacetate*, $CH_2I\cdot CO_2\cdot C_{10}H_{19}$, prepared by boiling *l*-menthyl chloroacetate with potassium iodide in alcoholic solution, is obtained as a colourless oil, b. p. 165°/22 mm., $[\alpha]_D^{20}$ $-47\cdot29°$, which gradually becomes brown, and reacts with methylethyl*iso*butylamine, forming the *hydriodide*, $NMeEtBu^\beta,HI$, m. p. 132°.

The *additive product* of methyl*iso*butylbenzylamine and *l*-menthyl iodoacetate is obtained as an amorphous mass, which on recrystallisation from a mixture of acetone and ether yields a colourless powder, $C_{24}H_{40}O_2NI$, decomp. 151·5°, $[\alpha]_D$ $-28\cdot97°$; the mother liquor from this yields an optically inactive, amorphous *salt* of the same composition, which evolves menthol when heated with potassium hydroxide.

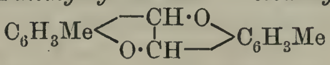
The *additive product* of *l*-menthyl iodoacetate and *N*-ethyltetrahydro*iso*quinoline, when recrystallised from a mixture of acetone and ethyl acetate, yields two quaternary *iodides*,



$$C_6H_4{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\end{matrix}{>}NEtI\cdot CH_2\cdot CO_2\cdot C_{10}H_{19};$$

the less soluble iodide crystallises in glistening scales, decomp. 183°, $[\alpha]_D$ $-44\cdot87°$, and, when gently heated with potassium hydroxide in alcoholic solution, yields menthol and an inactive *betaine*, decomp. 232°. The more soluble iodide forms a crystalline powder, decomp. 155°, $[\alpha]_D$ $-17\cdot54°$, and, when heated with potassium hydroxide, yields menthol and an optically inactive *betaine*, decomp. 223°. When shaken with moist silver oxide in alcoholic solution, the iodide, decomp. 153°, yields menthol and a *betaine*, $\alpha+0\cdot21°$ (100 mm. tube), whilst under the same conditions the iodide, decomp. 183°, yields menthol and a *betaine*, α $-0\cdot19°$ (100 mm. tube); the solutions of these two betaines become optically inactive in two days. G. Y.

Reduction Products of Schiff's Bases. OTTO ANSELMINO (*Ber.*, 1908, **41**, 621—623. Compare Abstr., 1907, i, 913).—*o*-Hydroxy-*m*-methylbenzylideneaniline, $OH\cdot C_6H_3Me\cdot CH{:}NPh$, when reduced with sodium and alcohol or with zinc dust and glacial acetic acid at moderate temperatures, yields o-*hydroxy*-as-m-*xylylaniline*, $OH\cdot C_6H_3Me\cdot CH_2\cdot NHPh$, which crystallises from light petroleum in needles, m. p. 101°. Its N-*acetyl* derivative, $C_{16}H_{15}O_2N$, has m. p. 102°. When heated for some time with zinc dust and acetic acid, the benzylidene compound yields *di*-o-*hydroxy*-m-*methylhydrobenzoin diesoanhydride*,



$$C_6H_3Me<\begin{matrix}-CH\cdot O\\ \vert\\ O\cdot CH-\end{matrix}>C_6H_3Me$$

(compare Harries, Abstr., 1892, 168), which crystallises from alcohol in colourless needles, m. p. 172°, but is gradually transformed into an isomeride, m. p. 194°.

When reduced with aluminium amalgam in ethereal solution, the anil yields *di*-o-*hydroxy-di*-m-*methyldianilinodibenzyl*,

$$OH\cdot C_6H_3Me\cdot CH(NHPh)\cdot CH(NHPh)\cdot C_6H_3Me\cdot OH,$$

which crystallises from light petroleum and ether in compact, colourless prisms, m. p. 169°. The *tetra-acetyl* derivative, $C_{36}H_{36}O_6N_2$, is sparingly soluble in benzene, and has m. p. 262°.

Dianilinodibenzyl, $NHPh\cdot CHPh\cdot CHPh\cdot NHPh$, obtained in the same manner from benzylideneaniline, crystallises from methyl alcohol in plates, m. p. 139°, or in needles, m. p. 164°. *Diacetylanilinodibenzyl*, $C_{30}H_{28}O_2N_2$, decomposes above 300°. *Dibenzoylanilinodibenzyl*, $C_{40}H_{32}O_2N_2$, sublimes above 300°.

J. J. S.

Preparation of Diphenylamine Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 189939).—*Sodium* 2-*nitrodiphenylamine*-4 : 3′-*disulphonate*, $NO_2\cdot C_6H_3(NaSO_3)\cdot NH\cdot C_6H_4\cdot SO_3Na$, red prisms containing water of crystallisation, is obtained by heating sodium *o*-chloronitrobenzene-*p*-sulphonate and sodium metanilate in aqueous sodium carbonate at 140—145°. *Sodium* 4-*nitrodiphenylamine*-2 : 3′-*disulphonate* is produced in a similar manner from sodium-*p*-chloronitrobenzene-*o*-sulphonate.

G. T. M.

Ammonium Phenoxide. K. BUCH (*Ber.*, 1908, **41**, 692—695).—Ammonium phenoxide has not yet been isolated, owing to its easy hydrolysis. The hydrolysis constant has been obtained by mixing known quantities of phenol and ammonia together, and measuring the partial vapour pressure of the ammonia in such solutions by the dynamical method; the gas employed for driving off the ammonia was a mixture of hydrogen and oxygen. Four solutions were thus examined, in three of which there was complete solution, and the fourth contained so much phenol that there existed in the liquid two phases. The moisture in the phenol used was estimated by Koppeschaar's method (this Journ., 1877, i, 746). The hydrolysis constant was found to be 5·1, which agrees with the calculated value obtained from the dissociation constants of phenol and ammonia and the ionisation of water. The constant, however, decreases with increasing concentration, and the degree of dissociation can be calculated in the usual manner. In the saturated solution, 70% of the salt is dissociated. W. R.

Conditions of Formation of Phenolsulphonic Acids. Julius Obermiller (*Ber.*, 1908, **41**, 696—702. Compare Abstr., 1907, i, 910). —It has been found previously that low temperatures and dilution of the sulphuric acid favoured the production of the ortho-acid. The highest yield of ortho-acid, according to the experiments carried out with 100% sulphuric acid at temperatures varying from 0° to 20°, is 40%; with 1·5 parts of sulphuric acid at 15—20° in one and a-half hours the yield of ortho-acid was 40·7%, and the total yield of both acids 74%, whereas, after leaving overnight, the total yield was 98%, of which 35·4% was ortho-acid. Mercuric oxide has no effect on the reaction.

When the temperature was raised and the sulphuric acid contained sulphur trioxide, the yield of para-acid obtained as the magnesium salt varied from 71% to 85% when the acid employed varied from 70 to 20% SO_3 at 90—100°, disulphonic acid remained in the mother liquor. With monohydrate, an 85% yield of para-acid was obtained at 90—100°, and the mother liquor contained ortho-acid and unchanged phenol.

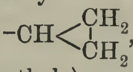
W. R

Synthesis of Phenols and Phenyl Ethers Containing the *iso*Allyl (Propenyl) Group. Auguste Béhal and Marc Tiffeneau (*Bull. Soc. chim.*, 1908, [iv], **3**, 301—310).—The object of this investigation was to effect the syntheses of propenylphenols and propenylphenyl ethers by reactions, such as that of Grignard, which take place at the atmospheric temperature, thus avoiding any risk of intramolecular migration. The following substances were prepared by the Grignard reaction, using the appropriate aldehyde and a magnesium alkyl haloid, usually magnesium ethyl iodide or bromide (compare Klages, Abstr., 1902, i, 609; 1905, i, 344). In some instances, a bimolecular compound (dimeride) is produced simultaneously. *p*-Propenylphenol, $HO\cdot C_6H_4\cdot CH\colon CHMe$, b. p. 138—140°/14 mm., m. p. 93°, crystallises in spangles. Anethole (compare Abstr., 1901, i, 272) is formed without any anisylpropanol when excess of the magnesium ethyl iodide is used (compare Klages, Abstr., 1905, i, 344) together with a bimolecular substance, probably identical with Orndorff and Morton's dianethole (Abstr., 1900, i, 289). *p*-Propenylphenetole, b. p. 242°, m. p. 58—59°, yields a *dibromide*, m. p. 55°, and is formed along with a liquid bimolecular substance, b. p. 233°/14 mm., and D^0 1·0366, probably containing a dimeride, derived from *cyclo*butane, and a noncyclic ethylenic dimeride.

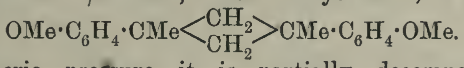
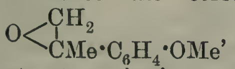
Propenylcatechol $[CH\colon CHMe : OH : OH = 1 : 3 : 4]$ cannot be prepared by the action of protocatechualdehyde on magnesium ethyl iodide, this reaction yielding a *phenol*, b. p. 155—160°/16 mm., m. p. 87—88°, which is crystalline and gives a green coloration with ferric chloride, and is probably a physical isomeride of the substance sought, which has m. p. 48—49° (Schimmel's Report, October 1907, 20) and occurs in betel oil. Other substances prepared were *iso*eugenol, *iso*chavibetol (compare Pomeranz, Abstr., 1901, i, 699), and propenyl-veratrole [$CH\colon CHMe : OMe : OMe = 1 : 3 : 4$], b. p. 260—263°, D^0 1·0711, and D^{20} 1·0551 (compare Moureu, Abstr., 1897, i, 403).

T. A. H.

Phenolic Ethers Containing the ψ-Allyl Side-chain $\cdot CMe\colon CH_2$. I. Preparation, Properties, and Nomenclature. II. Anisic and Homoanisic Series. Auguste Béhal and Marc Tiffeneau (*Bull. Soc. chim.*, 1908, [iv], 3, 310—314, 314—321).—An extension of the work described in the preceding abstract. The ethers are prepared by the action of excess of magnesium methyl iodide on cyclic alkyl esters. If insufficient of the Grignard reagent be employed, tertiary alcohols of the type $CRMe_2\cdot OH$ are also produced. Many of the results given have been recorded previously (Abstr., 1901, i, 246; 1904, i, 742; 1905, i, 883).

The best nomenclature for the allyl and propenyl ethers is probably that in which the aromatic radicle is regarded as substituted in the olefinic hydrocarbon, so that anethole, $OMe\cdot C_6H_4\cdot CH\colon CHMe$, becomes α-anisyl-$\Delta^\alpha$-propylene, and eugenol, $OH\cdot C_6H_3(OMe)\cdot CH_2\cdot CH\colon CH_2$, α-vanillyl-$\Delta^\beta$-propylene and so on, but it is probably more convenient to extend the system at present in use and use the prefix *pseudo* to distinguish those ethers containing the *pseudo*-allyl chain and *cyclo* the possible isomerides containing the group  $-CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, giving, for example, the series estragole, *iso*estragole (anethole), *pseudo*estragole, and *cyclo*estragole. A third possibility is to use the names of the substituent olefinic radicles, thus: allyl, *iso*allyl, *pseudo*allyl, and *cyclo*allyl.

o-ψ-Propenylanisole, $MeO\cdot C_6H_4\cdot CMe\colon CH_2$, may be obtained by methylating *o-ψ-propenylphenol*, b. p. 204°, D^0 1·0528 (itself prepared by the action of magnesium methyl iodide on methyl salicylate), or directly by the action of magnesium methyl iodide on methyl *o*-methoxybenzoate (Abstr., 1904, i, 742).

m-Methoxyphenyldimethylcarbinol, $OMe\cdot C_6H_4\cdot CMe_2\cdot OH$, the intermediate product obtained by the action of magnesium methyl iodide on methyl *m*-methoxybenzoate, has b. p. 242°/770 mm. Methyl *p*-methoxybenzoate, treated by the general method, yields in addition to *p*-ψ-propenylanisole (*loc. cit.*) a small quantity of the liquid ether, $O(CMe_2\cdot C_6H_4\cdot OMe)_2$, b. p. 260—270°/31 mm., and a *dimeride*, m. p. 58°, b. p. 210—215°/15 mm., which is crystalline, and may have the constitution  $OMe\cdot C_6H_4\cdot CMe<\begin{matrix}CH_2\\CH_2\end{matrix}>CMe\cdot C_6H_4\cdot OMe$. On distillation at atmospheric pressure, it is partially decomposed into *p*-ψ-propenylanisole and some *iso*propylanisole. *p*-ψ-Propenylanisole, on treatment with iodine and yellow mercuric oxide, yields an iodohydrin, which with potassium hydroxide (Abstr., 1905, i, 883) furnishes the corresponding *ethylene oxide* (ψ-estragole oxide),  $O<\begin{matrix}CH_2\\|\\CMe\cdot C_6H_4\cdot OMe\end{matrix}$, b. p. 130—135°/12 mm., and this on distillation at atmospheric pressure passes into *p*-methoxyhydratropaldehyde (Bougault, Abstr., 1902, i, 452), the semicarbazone of which exists in two forms, having m. p. 134° and m. p. 207—208° (compare Balbiano and Paolini, Abstr., 1906, i, 186). The aldehyde itself on keeping forms a *trimeride*, m. p. 103—104° or 106°.

p-ψ-*Propenylphenetole*, $OEt\cdot C_6H_4\cdot CMe\!:\!CH_2$, m. p. 27—28°, b. p. 113—114°/13 mm., or 234—235°/760 mm., D^{31} 0·969, n_D^{24} 1·540536, similarly obtained from ethyl *p*-ethoxybenzoate, b. p. 274—275°, or 148—149°/14 mm., D^{21} 1·076, by the general reaction, crystallises readily from alcohol. The *dimeride*, m. p. 74°, simultaneously formed, is partially depolymerised on heating. *p-iso*Propylphenetole, obtained by reduction of *p*-ψ-propenylphenetole as already described (Abstr., 1905, i, 883), has D^{23} 0·9286 and n_D^{94} 1·4974. T. A. H.

Intramolecular Rearrangement Effected by Fusion with Potassium Hydroxide: The Action of Fused Potassium Hydroxide on Quinol and Catechol. JAN J. BLANKSMA (*Chem. Weekblad*, 1908, 5, 93—95. Compare following abstract; Barth and Schreder, Abstr., 1879, 633; Kauffmann, Abstr., 1907, ii, 214 and 519; Hantzsch, Abstr., 1907, ii, 418).—The author has investigated the action of potassium hydroxide on quinol and catechol at temperatures between 130° and 260°. Resorcinol is not formed, indicating that the intramolecular rearrangement resulting from fusion of certain disubstituted derivatives with potassium hydroxide does not take place after substitution by hydroxyl. A. J. W.

Intramolecular Rearrangement Effected by Fusion with Potassium Hydroxide: Behaviour of Chlorophenols and Bromophenols with Potassium Hydroxide, Zinc Chloride, Zinc Bromide, Sulphuric Acid, Potassium Carbonate, and Potassium Acetate. S. TYMSTRA (*Chem. Weekblad*, 1908, 5, 96—101. Compare foregoing abstract).—From the results of experiments on chlorophenols and bromophenols with the reagents named, the author concludes that the intramolecular rearrangement by which resorcinol is formed takes place under the influence of the alkali hydroxide simultaneously with the replacement of halogen by hydroxyl, and that potassium carbonate can effect the transformation into the corresponding dihydroxybenzene, but not the molecular rearrangement. A. J. W.

Preparation of 3-Aminoacetylcatechol. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 189483. Compare Abstr., 1907, i, 1049).—The *N*-benzoylaminoacetylcatechol ethers,

$$NHBz\cdot CH_2\cdot CO\cdot C_6H_3(OR)_2,$$

obtained by the interaction of hippuryl chloride and catechol ethers, are readily hydrolysed by aqueous mineral acids under pressure to 3-aminoacetylcatechol, which has the powerful hæmostatic properties of the active substances from the suprarenal capsules.

N-Benzoylaminoacetylveratrole, or the corresponding diethyl ether, when hydrolysed in an autoclave with concentrated hydrochloric acid or 30% sulphuric acid at 110° to 190° readily yields the required base. G. T. M.

Preparation of Mixed Alkyl Aromatic Ethers. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 189843).—The nitroso-derivatives of the mono- and di-alkylcarbamides alkylate phenols in the presence of alkalis.

Codeine is obtained by treating morphine with nitrosomethylcarbamide in alcoholic sodium methoxide. β-Ethoxynaphthalene is produced on adding nitrosodiethylcarbamide to a solution of β-naphthol in *N*-sodium hydroxide. Guaiacol is similarly obtained from catechol, sodium hydroxide, and nitrosomethylcarbamide in alcoholic solution, and may be further alkylated to veratrole by a repetition of this process.

The triethyl ether of pyrogallol can be produced by the action of nitrosodiethylcarbamide on pyrogallol dissolved in methyl-alcoholic sodium hydroxide. G. T. M.

p-**Iodoguaiacol.** Efisio Mameli and Giuseppe Pinna (*Chem. Zentr.*, 1907, ii, 2044; from *Arch. Farm. sperim.*, 1907, 6, 193. Compare this vol., i, 18).—A detailed description of the preparation of *p*-iodoguaiacol from *p*-aminoguaiacol by means of the Sandmeyer reaction. The result of experiments with iodoguaiacol on animals and its medicinal properties are given in the original. J. V. E.

Origin and Formation of Cholesterol. Isaac Lifschütz (*Zeitsch. physiol. Chem.*, 1908, 55, 1—7).—By the oxidation of pure oleic acid in acetic acid solution with potassium permanganate (5% solution in water diluted with four times the volume of glacial acetic acid), a minute quantity of unsaponifiable matter is obtained which gives the characteristic cholesterol reaction of Liebermann. The other products of the reaction are: (1) a mixture of palmitic and oleic acids, and (2) a mixture of acids insoluble in light petroleum. Of the latter acids, one, m. p. 82—85°, of which the potassium salt gives no precipitate with calcium chloride, gave an acid number 460; it appears to be an acid with several carboxylic acid groups. These acids, when submitted to oxidation again, yield small quantities of the substance which gives the cholesterol reactions. S. B. S.

Cholesterol. VI. Otto Diels and Karl Linn (*Ber.*, 1908, 41, 544—550).—The observation made by Diels and Abderhalden that cholesterol and cholestenone yield different cholestanols on reduction with sodium and amyl alcohol (Abstr., 1906, i, 272, 425; Neuberg, 1906, i, 356) has lead to their reinvestigation in view of the fact that the parent compounds possess the same nucleus (this vol., i, 164). That the two cholestanols are not stereoisomerides is shown by their forming different hydrocarbons on replacing the alcoholic hydroxyl, first by chlorine and then by hydrogen. Windaus' hypothesis that in the production of α-cholestanol from cholesterol and sodium amyloxide (Abstr., 1907, i, 610) the cholesterol merely undergoes an isomeric change, although in agreement with the production of two cholestanes, is not regarded as correct. Sodium amyloxide is actually a reducing agent, as cholestenone gives α-cholestanol after seven hours' heating, a noteworthy result, as reduction with sodium and amyl alcohol leads to the formation of the β-compound. Further, the inactivity of sodium ethoxide at 140° towards cholesterol is against the Windaus view, and the relationships of the compounds described is an open question.

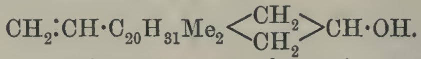
α-Cholestyl chloride, $C_{27}H_{47}Cl$, obtained by the action of phosphorus pentachloride, forms glistening leaflets, m. p. 116°, which on reduction with sodium and amyl alcohol yield *α-cholestane*, $C_{27}H_{48}$, forming long, glistening needles, m. p. 72°, and behaving as a saturated compound towards bromine.

β-Cholestyl chloride, $C_{27}H_{47}Cl$, forms rosettes of stout, white needles, softening at 89°, m. p. 92°, to a cloudy liquid which becomes clear at 100°. *β-Cholestane*, $C_{27}H_{48}$, forms needles, m. p. 80°; a mixture of the α- and β-compounds gives a m. p. showing a depression of 20°.

Neither of these hydrocarbons gives the cholesterol colour reactions.

W. R.

Cholesterol. X. ADOLF WINDAUS (*Ber.*, 1908, **41**, 611—621. Compare Abstr., 1907, i, 212, 610).—Previous researches on cholesterol point to the constitutional formula

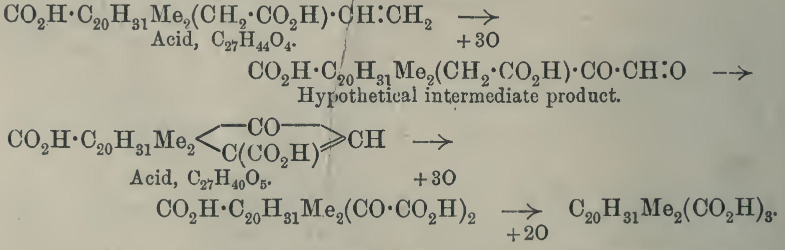


$$CH_2{:}CH\cdot C_{20}H_{31}Me_2{<}{\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}}{>}CH\cdot OH.$$

The present paper contains an account of experiments with the dibasic acid, $C_{27}H_{44}O_4$, obtained by Diels and Abderhalden (Abstr., 1903, i, 819; 1904, i, 880) by the action of potassium hypobromite on cholesterol. With three atoms of oxygen, the acid yields a dibasic acid, $C_{27}H_{40}O_5$, which readily takes up two atoms of hydrogen, yielding a crystalline, dibasic acid, $C_{27}H_{42}O_5$, the fifth oxygen atom in which is present in the form of a carbonyl group. When the acid, $C_{27}H_{40}O_5$, is oxidised with permanganate (3 atoms of oxygen), a tribasic acid, $C_{27}H_{40}O_8$, is obtained, which is also produced when the original acid, $C_{27}H_{44}O_4$, is oxidised with excess of permanganate (6 atoms of oxygen).

The tribasic acid contains at least one, and probably two, carbonyl groups, but no hydroxyl group, and when further oxidised yields a tribasic acid, $C_{25}H_{40}O_6$.

The following scheme represents the reactions:



$$\underset{\text{Acid, }C_{27}H_{44}O_4.}{CO_2H\cdot C_{20}H_{31}Me_2(CH_2\cdot CO_2H)\cdot CH{:}CH_2} \xrightarrow[+3O]{}$$

$$\underset{\text{Hypothetical intermediate product.}}{CO_2H\cdot C_{20}H_{31}Me_2(CH_2\cdot CO_2H)\cdot CO\cdot CH{:}O} \longrightarrow$$

$$\underset{\text{Acid, }C_{27}H_{40}O_5.}{CO_2H\cdot C_{20}H_{31}Me_2{<}{\begin{smallmatrix}—CO—\\C(CO_2H)\end{smallmatrix}}{\geqslant}CH} \xrightarrow[+3O]{}$$

$$CO_2H\cdot C_{20}H_{31}Me_2(CO\cdot CO_2H)_2 \xrightarrow[+2O]{} C_{20}H_{31}Me_2(CO_2H)_3.$$

The *acid*, $C_{27}H_{40}O_5$, is most readily purified by the recrystallisation of its normal sodium salt from dilute alcohol. The acid crystallises from dilute acetic acid in compact prisms, m. p. 216—217°. It yields a *monomethyl* ester, $C_{28}H_{42}O_5$, which crystallises from methyl alcohol in long prisms, m. p. 136—137°. The reduction *product*, $C_{27}H_{42}O_5$, obtained with the aid of zinc dust and acetic acid, crystallises from a mixture of chloroform and light petroleum in compact needles, m. p. 158—159°, and is isomeric with the dibasic ketonic acid, obtained by oxidation of cholestandione (Abstr., 1904, i, 49). The *acid methyl* ester, $C_{28}H_{44}O_5$, has m. p. 132°, and the *oxime*, $C_{27}H_{43}O_5N$, m. p. 230—231°.

The *acid*, $C_{27}H_{40}O_8$, is most readily obtained in a crystalline form by solution in glacial acetic acid and the addition of concentrated hydrochloric acid. It forms short, pointed prisms, decomposes at 230—231°, and forms colloidal solutions with water. It yields characteristic, crystalline *potassium hydrogen*, $C_{27}H_{38}O_8K_2$, and *rubidium hydrogen* salts, $C_{27}H_{38}O_8Rb_2$. The salts derived from the alkali-earth metals and the heavy metals are insoluble and amorphous. The *oxime*, $C_{27}H_{41}O_8N$, is amorphous, but yields an acid *potassium* salt, $C_{27}H_{39}O_8NK_2$, which crystallises in prisms.

The *acid*, $C_{25}H_{40}O_6$, crystallises from dilute acetic acid in felted needles containing $1H_2O$. The anhydrous acid is hygroscopic, sinters at 130°, and has m. p. 204—205° (decomp.). The *rubidium dihydrogen* salt, $C_{25}H_{39}O_6Rb$, and the corresponding *calcium* salt crystallise well. A crystalline *potassium* salt, $C_{50}H_{77}O_{12}K_3$, has also been prepared.

J. J. S.

The Cholesterol Group. IV. Angelo Menozzi (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 91—94. Compare Abstr., 1903, ii, 385).—The properties of the cholesterol of hens' eggs and of its derivatives are identical with those of the cholesterol of bile and of its corresponding compounds.

T. H. P.

The Cholesterol Group. Bombicesterol, a New Member Existing in the Chrysalis of the Silkworm, Bombyx mori. V. Angelo Menozzi and A. Moreschi (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 95—99. Compare preceding abstract).—The authors have isolated from the chrysalis of the silkworm a member of the cholesterol group which differs in its properties from the cholesterol of bile and which they term bombicesterol.

Bombicesterol, $C_{26}H_{43}\cdot OH,H_2O$, crystallises in pointed, elongated, monoclinic or trimetric laminæ, m. p. 148°, $[\alpha]_D^{15} - 34°$. The *formate*, $H\cdot CO_2\cdot C_{26}H_{43}$, crystallises from a mixture of alcohol and ether in elongated laminæ, m. p. 101°, $[\alpha]_D^{17\cdot5} - 47°$, and the *acetate*, $C_{26}H_{43}OAc$, separates in laminæ, m. p. 129°, $[\alpha]_D^{17\cdot5} - 42\cdot7°$; the *benzoate*, $C_{26}H_{43}OBz$, crystallises in slender laminæ, m. p. 146°, $[\alpha]_D^{20} - 14\cdot63°$. The *salicylate*, m. p. 173—174°, and the *dibromo*-derivative, m. p. 111°, were also prepared. Treatment of an ethereal solution of bombicesterol with an acetic acid solution of bromine (1 mol.) yields two dibromoacetates differing in solubility; on reduction with zinc dust and acetic acid, the less soluble form yields an acetate, m. p. 114°, which is that of ordinary cholesterol acetate, whilst the more readily soluble form gives an acetate, m. p. 129°.

T. H. P.

Attempt to Synthesise Propionylimino*cyclo*heptanecarboxylic Acid. George L. Stadnikoff (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 142—150. Compare this vol., i, 251).—The synthesis of this acid was undertaken firstly in order to determine the limit of applicability of the general method proposed previously (compare Abstr., 1906, i, 425), and secondly, to see whether the imino-group of the acid is hydrolysed by mineral acids. On treating ethyl amino*cyclo*heptanecarboxylate with potassium cyanide and acetaldehyde, the first product of the reaction, $CN\cdot CHMe\cdot NH\cdot C_7H_{12}\cdot CO_2Et$, decomposes, forming α-aminopropionic acid and iminodipropionic acid, amino*cyclo*heptanecarboxylic acid also being produced. The latter, when similarly treated, produces *ethyl cyanoethyliminocyclo*heptanecarboxylate hydrochloride*,

$$CN\cdot CHMe\cdot NH\cdot C_7H_{12}\cdot CO_2Et,HCl,$$

m. p. 141—143° (decomp.), soluble in alcohol and water, insoluble in ether, and decomposing on hydrolysis into an amino- and an hydroxy-acid.

The aqueous solution, after the extraction of the imino-acid, yielded with hydrochloric acid α-aminopropionic acid, an isomeric form of iminodipropionic acid, carbon dioxide and monoxide, and a mixture of volatile alcoholic substances. The mechanism of the reaction is discussed, the explanation given being similar to that proposed previously for other like cases. Z. K.

Preparation of Alkylaminoalkyl Benzoates. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 190688).—The halogenated alkyl benzoates react with the secondary aliphatic amines to furnish dialkylaminoalkyl benzoates, which are of value as anæsthetics.

Diethylaminoethyl benzoate, $C_6H_5\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$, oil, b. p. 132°/5 mm.; the hydrochloride, colourless needles from alcohol-ether, m. p. 124°, is prepared by heating chloroethyl benzoate and diethylamine at 100—120° for twelve hours. The following are similarly obtained: *dimethylaminoethyl benzoate*, $C_6H_5\cdot CO_2\cdot CH_2\cdot CH_2\cdot NMe_2$, oil; hydrochloride, lustrous needles, m. p. 148°; *diisoamylaminoethyl benzoate*, oil; *hydrogen oxalate*, needles, m. p. 158°; *hydrochloride*, needles, m. p. 107—108°; *diethylaminoethyl benzoate*, oil; *picrate*, yellow needles, m. p. 146°. G. T. M.

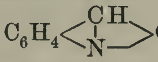
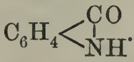
Preparation of Dimethylamino*iso*propyl Benzoate. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 189482. Compare Abstr., 1906, i, 952).—*Dimethylaminoisopropyl benzoate*,

$$C_6H_5\cdot CO_2\cdot CMe_2\cdot NMe_2,$$

heavy oil, sparingly soluble in water, is obtained as its hydrochloride, leaflets, m. p. 127—128°, by benzoylating dimethylamino*iso*propyl alcohol with benzoic anhydride or benzoyl chloride and extracting the product with hydrochloric acid. G. T. M.

Preparation of Alkylaminoalkyl *p*-Aminobenzoates. EMANUEL MERCK (D.R.-P. 189335).—The chloroethyldialkylamines having the general formula $NRR'\cdot CH_2\cdot CH_2Cl$ react with the salts of *p*-aminobenzoic acid to furnish the corresponding dialkylaminoalkyl *p*-aminobenzoate, $NRR'\cdot CH_2\cdot CH_2\cdot CO_2\cdot C_6H_4\cdot NH_2$.

Diethylaminoethyl p-*aminobenzoate hydrochloride*, m. p. 156°, is obtained by heating at 120—130° an intimate mixture of chlorotriethylamine, $NEt_2\cdot CH_2\cdot CH_2Cl$, and sodium *p*-aminobenzoate; the resulting base being neutralised with dilute hydrochloric acid. G. T. M.

Constitution of Anthranil. V. GUSTAV HELLER [and, in part, OTTO NÖTZEL] (*J. pr. Chem.*, 1908, [ii], 77, 145—171. Compare Abstr., 1902, i, 779; 1903, i, 827; 1904, i, 160; 1905, i, 130).—An account of the work of various authors on the constitution of anthranil and a résumé of the evidence for and against the constitutional formulæ  $C_6H_4<\begin{array}{c}CH\\|\\N\end{array}>O$ and  $C_6H_4<\begin{array}{c}CO\\|\\NH\end{array}$. The following new experimental evidence in favour of the latter formula is described.

Anthranil is oxidised by potassium dichromate in nitric acid solution at 75°, forming *o*-azoxybenzoic acid (compare Bamberger, Abstr., 1903, i, 634), whereas methylanthroxan, under similar conditions, yields *o-nitrosoacetophenone*, $NO\cdot C_6H_4\cdot COMe$, which crystallises in yellow prisms, m. p. 129° (decomp.), is converted into azoxyacetophenone by the action of dilute alkalis, or into azoxybenzoic acid by oxidation with potassium permanganate, yields a red *oil* (*o-acetoazobenzene*?) when heated with aniline in 50% acetic acid, and again forms methylanthroxan on reduction with zinc dust and acetic acid or sodium hydroxide. The action of benzoyl chloride on anthranil in pyridine solution at −10° leads to the formation of a yellowish-red *resin*, which contains 2·45% of chlorine, and is probably a mixture of several substances, together with benzoic acid and benzoylanthranil; the resin cannot be converted into benzoylanthranil or benzoylanthranilic acid. Anthranil is not formed when anthroxanic acid is decomposed by prolonged heating at 190°, by heating in a vacuum, or by prolonged boiling in cumene solution. When treated with sodium nitrite in hydrochloric acid solution below −15°, anthranil forms a *nitrosoamine*, $C_7H_4O_2N_2,H_2O$, which crystallises in needles and rapidly decomposes when dried. Whilst anthranil does not react with hydrogen cyanide, isatin forms an additive *compound*, $C_9H_6O_2N_2$, which separates from acetone-light petroleum in colourless crystals, and decomposes evolving hydrogen cyanide and yielding isatin when heated or boiled with water.

Methylanthroxan does not react with phenylhydrazine or with benzoyl chloride in pyridine solution. When heated with an excess of benzoyl chloride at 140—150°, it forms small amounts of a *substance*, crystallising in red needles, m. p. 178°. Whilst anthranil yields isatoic acid when heated with ethyl chlorocarbonate in high-boiling petroleum solution, methylanthroxan, under the same conditions, remains unchanged. Contrary to Bamberger's statement (Abstr., 1904, i, 422), methylanthroxan is almost unattacked when boiled for one hour with 7% aqueous sodium hydroxide. It reacts slowly with methyl sulphate, forming a *product*, which yields an amorphous *picrate*, and a *platinichloride*, decomp. above 240°. G. Y.

[Properties, Detection and Estimation of] "Saccharin." GIOVANNI PARMEGGIANI (*Boll. chim. farm.*, 1908, 47, 37—38).—The author's work clears up various disputed points concerning the properties of *o*-benzoicsulphinide.

o-Benzoicsulphinide has m. p. 220°, and dissolves in 400 parts of water at the ordinary temperature and in amyl acetate and ethyl acetate to the extents of 1 : 50 and 1 : 20 respectively. It is not attacked by nascent hydrogen in alkaline solution, by potassium permanganate, by hydrogen peroxide, or by halogens in the cold. Cold nitric acid does not attack it, but, when heated with the acid, it undergoes hydrolysis, the sulpho-group being oxidised to sulphuric acid. The most sensitive precipitant for *o*-benzoicsulphinide is aqueous mercurous nitrate, the precipitate formed with mercuric nitrate being less abundant and soluble in excess of the reagent. Neutral solutions of the sulphinide precipitate solutions of salts of quinine or brucine, but not those of strychnine, morphine, or cocaine. The white, waxy condensation product of *o*-benzoicsulphinide with formaldehyde is unstable at a low heat, whilst the products formed with phenol, resorcinol, phloroglucinol, thymol, and α- and β-naphthols have no characters useful in the detection of the sulphinide.

The extraction of *o*-benzoicsulphinide from foods and its subsequent recognition may be effected as follows: 50 c.c. of the liquid are concentrated to about 25 c.c., acidified, if necessary, with hydrochloric or acetic acid, and extracted once with 30 c.c. of amyl acetate, which dissolves but little colouring matter from wines or liquors. The amyl acetate extract is separated, concentrated to a small volume, and defecated with a few drops of neutral lead acetate solution, the filtered liquid being then freed from lead by means of hydrogen sulphide and shaken with 20 c.c. of ethyl acetate. This extract is separated, evaporated to dryness on the water-bath, and the residue tested by tasting and other methods.

The following method of estimating *o*-benzoicsulphinide gives almost theoretical results. Fifty c.c. of the solution, after concentration and, if necessary, defecation as described above, are shaken several times with a total volume of 50 c.c. of a mixture, in equal volumes, of ether and light petroleum. The combined extracts are evaporated to dryness and the residue titrated with *N*/200 sodium hydroxide solution. T. H. P.

Preparation of Diphenylated Acid Amides by the Action of Diphenylcarbamide on Acids. JOHANNES HERZOG and V. HÂNCU (*Ber.*, 1908, 41, 636—637).—Diphenylated acid amides are formed when a mixture of acid and diphenylcarbamyl chloride is heated with anhydrous pyridine in a boiling-water bath. Carbon dioxide and hydrogen chloride are evolved, $R\cdot CO\cdot OH + COCl\cdot NPh_2 = R\cdot CO\cdot NPh_2 + HCl + CO_2$, and, after some ten minutes, the product is poured into water and recrystallised from alcohol. Diphenylbenzamide, m. p. 179—180°, and diphenylcinnamide, m. p. 156—157°, have been prepared. J. J. S.

Resolution of Racemic Amino-acids by Yeast. II. FELIX EHRLICH (and ADOLF WENDEL) (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 626, 198—222; *Biochem. Zeitsch.*, 1908, 8, 438—466).—Further examples of the resolution of amino-acids by yeast, in the presence of sugar, according to the method described (Abstr., 1906, i, 807). The optical antipodes of the naturally occurring amino-acids are thus obtained, but, by applying Walden's inversion, the natural substances are obtainable (Fischer, Abstr., 1907, i, 192).

d-Phenylalanine and *d*-serine have now been obtained from the synthetic racemic acids with specific rotations agreeing very closely with those given by Fischer; serine is the first amino-hydroxy-acid to be resolved by the yeast method.

α-Aminophenylacetic and α-amino-α-methylbutyric acids have been resolved for the first time. The highest specific rotation observed for l-*α-aminophenylacetic acid* was in water, $[\alpha]_D^{20}$ −90·35°, and in 10% hydrochloric acid, $[\alpha]_D^{20}$ −144·83°. The *l*-acid is more soluble than the *dl*-acid, which fact renders the isolation of the *l*-acid difficult and makes it somewhat uncertain whether the resolution was complete; the rotation is higher than that of any other known amino-acid (except cystine), and very much higher than that of the next homologue, phenylalanine. *l*-α-Aminophenylacetic acid melts at 293° in an open, and at 303—305° in a closed capillary tube (at very similar temperature to the *dl*-acid); the *hydrochloride* forms prisms, m. p. 242—244° and 235° in open and closed tubes respectively; the *phenylcarbimide*, $C_{15}H_{14}O_3N_2$, needles, m. p. 168°, $[\alpha]_D^{20}$ −129·27° in *N*/2 sodium hydroxide, and the *phenylhydantoin*, $C_{15}H_{12}O_2N_2$ (l-*diphenylhydantoin*), needles, m. p. 191°, lævorotatory, have also been prepared.

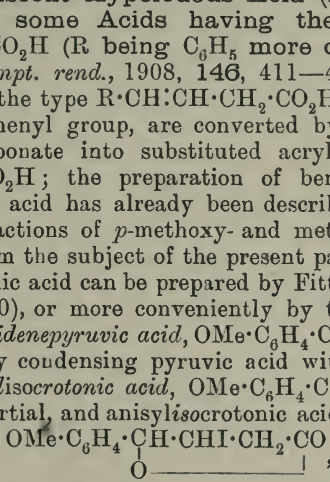
The highest specific rotation observed for l-*α-amino-α-methylbutyric acid* ("*iso*valine") was in water, $[\alpha]_D^{20}$ −9·10°, and in 20% hydrochloric acid, $[\alpha]_D^{20}$ −6·11°.

Attempts to resolve β-aminobutyric acid were wholly unsuccessful. Additional manipulative details regarding the method are given.

G. B.

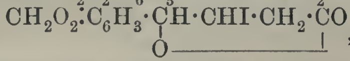
Action of Nascent Hypoiodous Acid (Iodine and Sodium Carbonate) on some Acids having the General Formula $R\cdot CH\colon CH\cdot CH_2\cdot CO_2H$ (R being C_6H_5 more or less substituted).

J. Bougault (*Compt. rend.*, 1908, **146**, 411—414).—Substituted *iso*crotonic acids of the type $R\cdot CH\colon CH\cdot CH_2\cdot CO_2H$, where R is a phenyl or substituted phenyl group, are converted by the action of iodine and sodium carbonate into substituted acrylic acids of the type $R\cdot CO\cdot CH\colon CH\cdot CO_2H$; the preparation of benzoylacrylic acid from phenyl*iso*crotonic acid has already been described (this vol., i, 179); the analogous reactions of *p*-methoxy- and methylenedioxy-phenyl*iso*crotonic acids form the subject of the present paper.

Anisyl*iso*crotonic acid can be prepared by Fittig and Politis' method (Abstr., 1890, 770), or more conveniently by the following series of reactions: *anisylidenepyruvic acid*, $OMe\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot CO_2H$, m. p. 131°, obtained by condensing pyruvic acid with anisaldehyde, yields *α-hydroxy-γ-anisyl*iso*crotonic acid*, $OMe\cdot C_6H_4\cdot CH\colon CH\cdot CH(OH)\cdot CO_2H$, m. p. 145°, on partial, and anisyl*iso*crotonic acid on further, reduction. The iodolactone,  $\begin{array}{l}OMe\cdot C_6H_4\cdot CH\cdot CHI\cdot CH_2\cdot CO\\ \hphantom{OMe\cdot C_6H_4\cdot }\underline{O\hphantom{H\cdot CHI\cdot CH_2\cdot C}}|\end{array}$, m. p. 125°, on treatment with excess of sodium carbonate is converted into *p*-methoxybenzoyl acrylic acid (anisoylacrylic acid), $OMe\cdot C_6H_4\cdot CO\cdot CH\colon CH\cdot CO_2H$, m. p. 134° (not 131° as previously stated, this vol., i, 179), which forms pale yellow needles, is decomposed by boiling with dilute alkalis into glyoxylic acid and *p*-methoxyacetophenone, and combines with HBr to form a *compound*, having m. p. 130°, or with aniline to form an *acid*, having m. p. 121°.

Piperonylidenepyruvic acid, m. p. 161° (Scholtz, Abstr., 1895, i, 469, gives 149—150°), on reduction yields *α-hydroxy-γ-methylenedioxyphenylcrotonic acid*, $CH_2O_2{:}C_6H_3\cdot CH{:}CH\cdot CH(OH)\cdot CO_2H$, m. p. 143°, and, finally, *methylenedioxyphenyl*isocrotonic *acid*,

$$CH_2O_2{:}C_6H_3\cdot CH{:}CH\cdot CH_2\cdot CO_2H;$$

the *iodolactone*,  $\underbrace{CH_2O_2{:}C_6H_3\cdot CH\cdot CHI\cdot CH_2\cdot CO}_{O}$, of this acid has m. p. 103°, and on treatment with sodium carbonate yields *methylenedioxybenzoylacrylic* (*piperonylacrylic*) *acid*, $CH_2O_2\cdot C_6H_3\cdot CO\cdot CH{:}CH\cdot CO_2H$, which forms sulphur-yellow crystals, darkens and decomposes at 180°, and melts at 200°; it combines with HBr to form a *compound* which decomposes before it melts, or, with aniline, to form an *acid* having m. p. 134°. M. A. W.

Liberation of Carbon Monoxide by Heating Acylchlorides.

Augustin Bistrzycki and August Landtwing (*Ber.*, 1908, **41**, 686—692. Compare Schmidlin and Hodgson, this vol., i, 170).—Experiments carried out with acids have shown that tertiary acids, like triphenylacetic acid, on dissolution in sulphuric acid, liberate carbon monoxide much more readily than monobasic primary acids (Abstr., 1907, i, 1039), and the research has been extended to the acyl chlorides. It has been found that a mixture of phosphorus pentachloride (1 part) and phosphoryl chloride (5 parts), when heated with the acid (1 part), leads to the formation of the acid chloride in good yield.

Triphenylacetyl chloride (Schmidlin and Hodgson, *loc. cit.*) when heated at 170—180° is decomposed almost quantitatively into carbon monoxide and chlorotriphenylmethane. *Diphenyl*-p-*tolylacetyl chloride*, $C_6H_4Me\cdot CPh_2\cdot COCl$, separates from light petroleum in crystalline aggregates, m. p. 89—90°, and when heated is also decomposed quantitatively above 120°. At 200°, hydrogen chloride is evolved quantitatively, and possibly *p*-tolylfluorene is left behind.

ββ-Di-p-*tolylpropionyl chloride*, $CMe(C_6H_4Me)_2\cdot COCl$, crystallising in flat prisms from light petroleum, m. p. 54·5—55·5°, is very stable towards water. At 220°, it is slowly decomposed into carbon monoxide, hydrogen chloride, and *as*-di-*p*-tolylethylene (Abstr., 1905, i, 285). Chlorodiphenylacetyl chloride (Bickel, Abstr., 1889, 999) at 280° loses carbon monoxide quantitatively, and somewhat less than half of its chlorine as hydrogen chloride.

The secondary chloride, diphenylacetyl chloride, m. p. 56—57° (Staudinger, Abstr., 1905, i, 444, gives 55°), loses carbon monoxide less completely and at a higher temperature than with the tertiary chlorides, and primary palmityl chloride gives only traces of an inflammable gas at 275°.

These results are therefore in agreement with those obtained with the acids themselves.

Triphenylacetamide, m. p. 238° (Schmidlin and Hodgson, *loc. cit.*, give 240—241°), at 300° gives a very small quantity of an inflammable gas. Methyl triphenylacetate at 250° gives neither ethylene nor carbon monoxide. W. R.

Action of Sulphosalicylic Acid on Sodium Diborate. LÉONCE BARTHE (*Compt. rend.*, 1908, **146**, 408—411).—*Sodium oxydiborodisulphosalicylate*. $O[B(OH)\cdot O\cdot C_6H_3(SO_3H)\cdot CO_2Na]_2$, is obtained in the form of magnificent colourless crystals containing $3H_2O$ when an aqueous solution of sodium diborate (1 mol.) is mixed with an alcoholic solution of sulphosalicylic acid (2 mols.); the following equation represents the reaction:

$$Na_2B_4O_7 + 2OH\cdot C_6H_3(SO_3H)\cdot CO_2H + 2H_2O = O[B(OH)\cdot O\cdot C_6H_3(SO_3H)\cdot CO_2Na]_2 + 2B(OH)_3.$$

The compound is a tetra-basic acid, it is a more delicate reagent for albumin than sulphosalicylic acid, and its solution gives a violet colour with ferric chloride. The *sodio-potassium* salt,

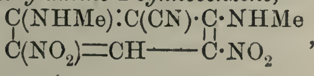
$$O[B(OH)\cdot O\cdot C_6H_3(SO_3K)\cdot CO_2Na]_2,$$

forms brilliant crystalline plates.

Sulphosalicylic acid reacts with sodium phosphate or arsenate to form crystalline derivatives. M. A. W.

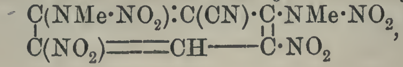
Constitution of Van Geuns' Dinitromethoxybenzonitrile. JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, **10**, 509—511).—The dinitromethoxybenzonitrile prepared by Van Geuns (*Diss.*, Amsterdam, 1903) by acting on 3-nitro-2-cyanoanisole with a mixture of nitric and sulphuric acids is shown to be 3 : 4-*dinitro*-2-*cyanoanisole*; it has m. p. 113°. The corresponding 3 : 4-*dinitro*-2-*cyanophenetole* has m. p. 63°. The 3-nitro-group in these two compounds may be readily replaced by OH, OMe, NH_2, NHMe, NHPh, &c. The constitution was determined as follows: the nitro-group in position 3 in dinitromethoxybenzonitrile, m. p. 113°, is replaced by an amino-group by heating the substance with alcoholic ammonia, since on removing the amino-group by diazotisation and boiling with alcohol a nitrocyanomethoxybenzene, m. p. 126°, is obtained, not identical with 3-nitro-2-cyanoanisole. The nitro-group in this compound must occupy position 4 or 6, since on nitration it yields 4 : 6-*dinitro*-2-*cyanoanisole*, m. p. 71°. The constitution of this compound was determined by converting it by means of alcoholic ammonia or methylamine into 4 : 6-dinitro-1-amino-2-cyanobenzene and 4 : 6-dinitro-1-methylamino-2-cyanobenzene respectively (compare Blanksma, Abstr., 1902, i, 281). That the nitro-group in the nitrocyanomethoxybenzene, m. p. 126°, occupies position 4 and not 6 is shown by its conversion into 5-nitrosalicylic acid by hydrochloric acid under pressure at 150°.

The compound obtained by the nitration of 2-cyano-1 : 3-dimethoxybenzene or 4-nitro-2-cyano-1 : 3-dimethoxybenzene (Van Geuns, *loc. cit.*) is 4 : 6-*dinitro*-2-*cyano*-1 : 3-*dimethoxybenzene*, since it is converted by hydrochloric acid at 150—160° into 4 : 6-dinitroresorcinol; it has m. p. 81°. Other new compounds which have been prepared have the following melting points: 4-*nitro*-3-*amino*-2-*cyanoanisole*, 180°; 4-*nitro*-2-*cyanoanisole*, m. p. 126°; 4 : 6-*dinitro*-1 : 3-*diamino*-2-*cyanobenzene*, m. p. 293°; 4 : 6-*dinitro*-1 : 3-*dimethylamino*-2-*cyanobenzene*,



$$\begin{array}{l} C(NHMe){:}C(CN)\cdot C\cdot NHMe \\ | \qquad\qquad\qquad\quad \| \\ C(NO_2){=}CH{-\!\!-}C\cdot NO_2 \end{array},$$

m. p. 232°; 4 : 6-*dinitro*-1 : 3-*dinitromethylamino*-2-*cyanobenzene*,



$$\begin{array}{l} C(NMe\cdot NO_2):C(CN)\cdot C\cdot NMe\cdot NO_2 \\ C(NO_2)=\!=\!=CH\text{——}C\cdot NO_2 \end{array},$$

m. p. 204°. W. H. G.

Benzylethyl-*m*-aminophenol and its Condensation with Esters of 1 : 3-Ketocarboxylic Acids to Coumarin Derivatives. Carl Bülow and Theodor Sprösser (*Ber.*, 1908, **41**, 487—497).—With the object of further investigating basic coumarins, benzylethyl-*m*-aminophenol has been obtained in a pure state (compare Gnehm and Scheutz, Abstr., 1901, i, 519) and condensed with ethyl acetoacetate, ethyl methylacetoacetate, and ethyl acetonedicarboxylate (compare Duisberg and von Pechmann, Abstr., 1883, 66; von Pechmann, Abstr., 1897, i, 220). The products obtained with ethyl acetoacetate and ethyl methylacetoacetate are respectively 7-benzylethylamino-4-methylcoumarin and 7-benzylethylamino-3 : 4-dimethylcoumarin, whilst instead of obtaining ethyl 7-benzylethylaminocoumarin-4-acetate with ethyl acetonedicarboxylate, the carbethoxyl group is eliminated during the reaction resulting in the formation of 7-benzylethylamino-4-methylcoumarin. Very dilute solutions of these basic coumarins exhibit a beautiful blue fluorescence.

Benzylethyl-*m*-aminophenol, directions for obtaining which in a pure form from the commercial product are given in the original, forms colourless crystals, m. p. 68°, which quickly turn violet on exposure to air and light; the *hydrochloride*, $C_{15}H_{17}ON,HCl,H_2O$, m. p. 91°, crystallises in rosette clusters; the *sodium* salt,

$$C_{15}H_{16}ONNa,2H_2O,$$

crystallises in white, silky leaflets, m. p. 120°; the *platinichloride*,

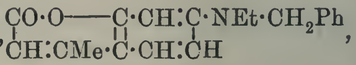
$$(C_{15}H_{17}ON)_2,H_2PtCl_6,2H_2O,$$

forms golden-yellow crystals, m. p. 186° (decomp.); the *ethyl ether*,

$$NEt(CH_2Ph)\cdot C_6H_4\cdot OEt,$$

is a yellow liquid, b. p. 250°/31 mm.

7-*Benzylethylamino*-4-*methylcoumarin*,



$$\begin{array}{l} CO\cdot O\text{——}C\cdot CH:C\cdot NEt\cdot CH_2Ph \\ CH:CMe\cdot C\cdot CH:CH \end{array},$$

crystallises in faintly coloured, rhombic leaflets, m. p. 88°.

7-*Benzylethylamino*-3 : 4-*dimethylcoumarin*, $C_{20}H_{21}O_2N$, forms colourless crystals, m. p. 116·5°. W. H. G.

Action of Free Hydroxylamine on Santonin. Luigi Francesconi and Guido Cusmano (*Atti R. Accad. Lincei*, 1907, [v], **17**, i, 64—73, 207—213).—The action of hydroxylamine on santonin in alkaline aqueous solution yields (1) santoninoxime, m. p. 216—219°; (2) *a-hydroxylaminosantoninoxime*, $C_{15}H_{22}O_4N_2$, which separates from water in massive, shining, apparently dimetric crystals, decomposing at 229—230° and melting at a few degrees higher; its aqueous solution is neutral and reduces Fehling's solution, gradually in the cold and immediately on heating, and potassium hydroxide solution and hydrochloric acid dissolve it, yielding liquids which reduce Fehling's solution vigorously.

When effected in methyl-alcoholic solution, the reaction yields the above *a*-compound and an isomeric *β-hydroxylaminosantoninoxime*,

$C_{15}H_{22}O_4N_2$, which crystallises from water or alcohol in elongated, monoclinic prisms, decomposing at 232—233°. When the original methyl-alcoholic solution is concentrated on the water-bath under diminished pressure, santoninoxime and the above β-compound are formed together with a *compound*, $C_{15}H_{27}O_6N_3$, which begins to undergo change at 170°, decomposes rapidly at about 230°, and is apparently the hydroxylamine salt of the acid corresponding with the β-compound; it decomposes Fehling's solution, slowly in the cold and rapidly on heating; it has a neutral reaction in aqueous solution, but gradually decomposes with formation of hydroxylamine and β-hydroxylaminosantoninoxime.

The *benzylidene* derivative of hydroxylammoniohydroxylaminosantoninoxime, $C_{22}H_{31}O_6N_3$, crystallises from alcohol or ethyl acetate in short, stout prisms, decomposing at 171—171·5°, and gives a violet colour with ferric chloride.

The *benzylidene* derivative of hydroxylaminosantoninoxime-β,

$C_{22}H_{26}O_4N_2$,

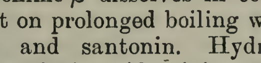
crystallises from methyl or ethyl alcohol, ethyl acetate, or ether in colourless, rectangular plates, which, at 140°, begin to decompose and evolve gas. The *benzoyl* derivative, $C_{29}H_{30}O_6N_2$, crystallises from methyl alcohol in hard, colourless prisms, m. p. 184° (decomp.).

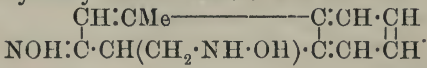
The *benzylidene* derivative of hydroxylaminosantoninoxime-α,

$C_{22}H_{26}O_4N_2$,

crystallises from aqueous alcohol in tufts of colourless prisms, m. p. 217° (decomp.), and does not reduce Fehling's solution in the cold.

When hydroxylaminosantoninoxime-α is dissolved in cold sodium hydroxide solution and the liquid mixed with a quantity of hydrochloric acid equivalent to the sodium hydroxide, the corresponding *santoninic acid*, $C_{15}H_{24}O_5N_2$, gradually separates; the acid crystallises from water in colourless, rectangular plates, which decompose at 140°, forming hydroxylaminosantoninoxime-α, and its aqueous solution has a strong acid reaction, reduces Fehling's solution, and gives no coloration with ferric chloride.

With dilute hydrochloric acid, hydroxylammoniohydroxylaminosantoninoxime gives, in the cold, hydroxylamine and hydroxylaminosantoninoxime-β, whilst in the hot, a mixture of santonin, hydroxylaminosantoninoxime-β, and santoninoxime is precipitated. Hydroxylaminosantoninoxime-β dissolves in cold hydrochloric acid practically unchanged, but on prolonged boiling with the acid it decomposes into santoninoxime and santonin. Hydroxylaminosantoninoxime-α dissolves in hydrochloric acid, giving a solution which readily yields hydroxylamine in the cold, and gradually deposits tufts of white needles, m. p. 200—201°, which were not further examined. Both the α- and β-hydroxylaminosantoninoximes, dissolved in water, chloroform, or methyl alcohol, undergo oxidation in presence of freshly-precipitated mercuric oxide, the solution becoming first pale yellow and later intensely reddish-yellow. The authors suggest for santonin the structure  $\begin{array}{l} CH{=}CMe{-}C{:}CH{\cdot}CH \\ |\qquad\qquad\;\; |\qquad\;\; || \\ CO{\cdot}C({:}CH_2){\cdot}C{:}CH{\cdot}CH \end{array}$, according to which it should yield a primary hydroxylamino-oxime of the formula



$$\begin{array}{l} \qquad\quad CH{:}CMe\text{————————}C{:}CH\cdot CH \\ NOH{:}C\cdot CH(CH_2\cdot NH\cdot OH)\cdot C{:}CH\cdot CH \end{array}$$

T. H. P.

Dialkylphthalides. I. 5-Amino- and 5-Hydroxy-diethylphthalide. Hugo Bauer (*Ber.*, 1908, **41**, 503—508).—The position of the nitro-group in nitrodiethylphthalide (Abstr., 1904, i, 417) has been determined in the following way. The amino-compound, obtained by reduction, is converted into the hydroxy-derivative, the methyl ether of which yields *m*-hydroxybenzoic acid when fused with potassium hydroxide (compare Gucci, Abstr., 1898, i, 257). The nitro-group is therefore in position 3 or 5 with reference to the carbonyl group. To ascertain which, aminodiethylphthalide is oxidised to the azo-compound, and this reduced to the hydrazo-compound; the last is partly reduced to the amine and partly oxidised to the azo-compound by concentrated mineral acids, a reaction characteristic of hydrazo-compounds which are symmetrically substituted in the para-positions. The nitro-group is therefore in position 5.

5-*Aminodiethylphthalide*, $NH_2\cdot C_6H_3<\substack{CEt_2\\CO}>O$, m. p. 165°, crystallises in colourless needles and forms a blue, fluorescent solution in methyl or ethyl alcohol; the *platinichloride* and the *acetyl* derivative, m. p. 121·5—122·5°, are described. 5-*Hydroxydiethylphthalide*, m. p. 129·5—130·5°, forms a *benzoyl* derivative, m. p. 101°, and a *methyl ether*, m. p. 79—80°, and by nitration yields 4 : 6-*dinitro-5-hydroxydiethylphthalide*, $OH\cdot C_6H(NO_2)_2<\substack{CEt_2\\CO}>O$, m. p. 169°, which forms intensely yellow solutions in alkali hydroxides or carbonates; the *methyl ether*, obtained by nitrating 5-methoxydiethylphthalide, has m. p. 131°, and by reduction yields 4 : 6-*diamino-5-methoxydiethylphthalide*, m. p. 205—206°, the *diacetyl* derivative of which has m. p. 131·5—132°.

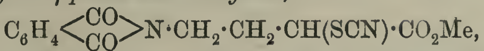
5-*Azodiethylphthalide*, $O<\substack{CEt_2\\CO}>C_6H_3\cdot N{:}N\cdot C_6H_3<\substack{CEt_2\\CO}>O$, m. p. 174—175°, forms orange-yellow leaflets, and is reduced by alcoholic ammonium sulphide to the *hydrazo*-compound, which crystallises in colourless needles, turns yellow at 190°, and has m. p. 206—208°.

C. S.

Derivatives of γ-Aminobutyric Acid. Siegmund Gabriel and James Colman (*Ber.*, 1908, **41**, 513—521. Compare Abstr., 1907, i, 625).—The paper merely contains an account of the following substances.

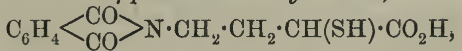
γ-Cyanopropylphthalimide (Abstr., 1890, 360, 1129) is hydrolysed by concentrated sulphuric acid, yielding, according to the conditions employed, γ-*phthaliminobutyramide*, $C_6H_4<\substack{CO\\CO}>N\cdot[CH_2]_3\cdot CO\cdot NH_2$, m. p. 165—166°, or γ-*phthaliminobutyric acid*, $C_{12}H_{11}O_4N$, m. p. 117—118°, sintering at 115°; the *methyl* ester has m. p. 89—90°, and the *ethyl* ester, m. p. 71—72°. By bromination in the presence of red phosphorus, the acid yields Fischer's α-bromo-γ-phthaliminobutyric acid (Abstr., 1901, 674), the *methyl* ester of which, m. p.

76—77°, reacts with boiling alcoholic potassium thiocyanate to form *methyl α-thiocyano-γ-phthaliminobutyrate*,



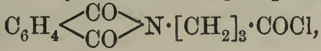
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH(SCN){\cdot}CO_2Me,$$

m. p. 88—89°. By hydrolysis with concentrated sulphuric acid, this compound yields *α-thiol-γ-phthaliminobutyric acid*,



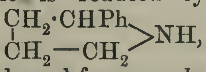
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH(SH){\cdot}CO_2H,$$

m. p. 139—140°. Hydrolysis of this acid by 20% boiling hydrochloric acid, or of methyl α-thiocyano-γ-phthaliminobutyrate by acetic and concentrated hydrochloric acids at 140°, leads to the formation of a colourless syrup, which exhibits the reactions of an aminomercaptan and consists probably of the hydrochloride of γ-amino-α-thiolbutyric acid, the homologue of *iso*cystein. To obtain a crystalline derivative, the syrup is treated with bromine water, whereby *γ-amino-α-sulphobutyric acid*, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(SO_3H){\cdot}CO_2H$, m. p. 263° (decomp.), is obtained.

γ-Phthaliminobutyric acid and phosphorus pentachloride yield the acid *chloride*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N{\cdot}[CH_2]_3{\cdot}COCl$, m. p. 67—69°, which reacts with boiling benzene in the presence of aluminium chloride to form *γ-phthaliminobutyrophenone*, $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N{\cdot}[CH_2]_3{\cdot}COPh$, m. p. 132—133°. The ketone is hydrolysed by acetic and concentrated hydrochloric acids at 150—155°, and yields the *hydrochloride*, $C_{10}H_{11}N,HCl$, which sinters at 200°, and melts at 210° to a turbid red liquid, which becomes clear at 211—212°; the *platinichloride*, $(C_{10}H_{11}N)_2,H_2PtCl_6$ darkens at 200° and has m. p. 220° (decomp.). The free *base*, $C_{10}H_{11}N$, m. p. 44—45°, b. p. 249°/752 mm., has a bitter taste, alkaline reaction, odour of phenyloxazoline, and forms a *picrate*, m. p. 198° (decomp.). The analysis of the base and of its salts shows that in the preceding hydrolysis the expected γ-aminobutyrophenone has lost a molecule of water, forming 2-*phenylpyrroline*. An analogous formation of 2-methylpyrroline and of 1:2-dimethylpyrroline has been observed by Hielscher (Abstr., 1898, i, 338). The pyrroline ring is readily ruptured when 2-phenylpyrroline is shaken with benzoyl chloride and sodium hydroxide, whereby *γ-benzoylaminobutyrophenone*,

$$NHBz{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COPh,$$

m. p. 125—126°, is produced (compare Markwalder, Abstr., 1907, i, 637). Similarly, phthalic anhydride at 210° converts 2-phenylpyrroline into γ-phthaliminobutyrophenone, mentioned above.

2-Phenylpyrrolidine is reduced by tin and hydrochloric acid to 2-*phenylpyrrolidine*,  $\left.\begin{array}{l}CH_2{\cdot}CHPh\\ CH_2{-}CH_2\end{array}\right>NH$, b. p. 241°/771 mm., which absorbs carbon dioxide and forms a *platinichloride*,

$$(C_{10}H_{13}N)_2,H_2PtCl_6,$$

m. p. 187—188°, an *aurichloride*, $C_{10}H_{13}N,HAuCl_4$, m. p. 110°, and a *picrate*, m. p. 148—149°. C. S.

Tautomerism of Cyclic Monoketones. CARL MANNICH and V. H. HÂNCU (*Ber.*, 1908, **41**, 564—575).—Whereas cyclic triketones and diketones have pronounced tautomeric properties, the only cyclic monoketone hitherto examined from this point of view is *cyclo*hexanone (Mannich, Abstr., 1906, i, 432). A number of cyclic monoketones are now found to react in a second tautomeric modification provided they contain a simple ring system. It requires, however, the influence of a very active reagent, such as acetic anhydride, to bring about the formation of derivatives of the enolic isomeride. On hydrolysis of such enolic esters, the corresponding ketones are re-formed, and no evidence could be gained that the enolic isomeride was even for a moment produced.

From *cyclo*hexanone, acetic anhydride and sodium acetate, the acetate of *cyclo*hexenol is produced; it is a colourless, oily liquid of a fruity odour, and forms adipic acid when oxidised with nitric acid, and not a nitro-derivative. Hydrogen bromide causes the formation of a ketone, $C_{12}H_{18}O$, b. p. 136—138°/10 mm. (*loc. cit.*), and not an additive product. The *acetate* of 1-methyl-Δ^3-*cyclo*hexene-4-ol is a colourless, oily liquid of a fruity odour, b. p. 191—192°, and gives β-methyladipic acid on oxidation. Hydrogen bromide converts it into a *ketone*, $C_{14}H_{22}O$, b. p. 157—159°/13 mm., formed by the elimination of water from two molecules of 1-methyl*cyclo*hexane-4-one. The *oxime* softens at 155°, m. p. 164°.

The *acetate* of 1-methyl-$\Delta^{1(\text{or }2)}$-*cyclo*hexene-2-ol is a colourless liquid of pleasant odour, b. p. 185—186°. The corresponding derivative of the tautomeric form of 1-methyl*cyclo*hexane-3-one has b. p. 195—196°.

The *acetate* of 1-methyl-4-*iso*propyl-$\Delta^{2(\text{or }3)}$-*cyclo*hexene-3-ol, prepared from *l*-menthone, is an oily, almost colourless liquid of a faint, but not menthone-like, odour, and has α_D +13·3° (200 mm. tube). A dextrorotatory menthone was obtained on hydrolysis. *l*-Menthone is known to pass over into *d*-menthone when treated with acids, and Beckmann (Abstr., 1889, 721) assumed intermediate formation of enol to explain this, an explanation confirmed by these observations. The corresponding *benzoate acid* is an oily liquid, b. p. 200—202°/30 mm. The *acetate* of Δ^1-*cyclo*pentene-1-ol is a colourless liquid of characteristic odour, b. p. 156—158°; on oxidation with permanganate in alkaline solution it yields glutaric acid. The *acetate* of Δ^1-*cyclo*heptene-1-ol, prepared from suberone, is a colourless liquid of refreshing odour, b. p. 194—196°. The action takes place less easily in ketones with five or seven units in the ring than with six. The *propionate* of Δ^1-*cyclo*hexene-1-ol, formed by heating *cyclo*hexanone with propionic anhydride, has b. p. 195—197°; the corresponding *butyrate* has b. p. 214—216°; both ethers are colourless, oily liquids of a fruity odour.

No trace of an enolic ether could be obtained from acetone, but mesityl oxide was formed by the interaction of acetone and acetic anhydride. It was not found possible to prepare methyl derivatives of the enolic form of *cyclo*hexanone. Pulegone and carvone react in the enolic form, but the change is complicated by secondary reactions, so that the pure ethers could not be isolated. Camphor does not react in the enolic form. Two isomerides of 1:2- and 1:3-methyl*cyclo*hexanones and menthone derivatives are possible according to the position of the double linking in the benzene nucleus, and the ethers prepared may represent mixtures of two very similar isomerides. E. F. A.

Chemical Action of Light. XI. GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 179—187, *Ber.*, 1908, **41**, 1071—1080. Compare Abstr., 1907, i, 587).—Like menthone, *cyclo*hexanone and the three isomeric methyl*cyclo*hexanones are hydrolysed by the action of light, the ring structure being broken down and a fatty acid, $C_nH_{2n}O_2$, and the corresponding unsaturated aldehyde, $C_nH_{2n-2}O$, being formed.

Thus, in aqueous or aqueous-alcoholic solution, *cyclo*hexanone yields hexoic acid and the hexylene aldehyde, $CH_2{:}CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO$.

1 : 2-Methyl*cyclo*hexanone hydrolyses to *n*-heptoic acid (œnanthoic acid) and Δ^{δ}-heptenaldehyde, $CHMe{:}CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHO$.

1 : 3-Methyl*cyclo*hexanone yields a heptoic acid, b. p. 215—216°, having the constitution $CHMe_2\cdot[CH_2]_3\cdot CO_2H$ or

$$CH_2Me\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H.$$

1 : 4-Methyl*cyclo*hexanone gives γ-*methylhexoic acid*,

$$CH_2Me\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO_2H,$$

b. p. 217—218°, and an aldehyde, $CH_2{:}CH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHO$ (?).

The presence of chlorophyll in the solutions retards the hydrolytic action of light in the cases examined, namely, acetone, *cyclo*hexanone, and menthone. T. H. P.

Spontaneous Transformation of Benzophenoneoxime. MICHAEL KONOWALOFF and K. MÜLLER (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1125—1126. Compare Holleman, Abstr., 1895, i, 475).—Having prepared benzophenoneoxime, m. p. 139—140°, in the ordinary way, it was found to have changed into a yellow liquid after remaining loosely corked for three and a-half years. The liquid consists of water, benzophenone, toluene, nitrotoluene, a small quantity of oxides of nitrogen, and possibly also benzene and its nitro-derivatives. When freshly-prepared benzophenoneoxime is allowed to remain in a loosely-corked flask, it becomes liquid in about fifteen days, and nitrogen oxides are evolved. Z. K.

Reciprocal Displacement of Hydrocarbon Groups in Friedel and Crafts' Reaction. HENRI DUVAL (*Compt. rend.*, 1908, **146**, 341—343).—With the intention of applying to its 2 : 2′-diamino-derivative the reaction previously described (Abstr., 1907, i, 663), the author has prepared 4 : 4′-diacetyldiphenylmethane. When diphenylmethane in carbon disulphide solution is treated with acetyl chloride in the presence of aluminium chloride, there are formed acetyldiphenylmethane, 4 : 4′-diacetyldiphenylmethane, and a considerable quantity of acetophenone. The latter can only have been formed by the displacement of the benzyl by the acetyl group under the influence of the aluminium chloride. Such a reaction has not previously been described under these conditions and at a low temperature. 4 : 4′-*Diacetyldiphenylmethane*, $COMe\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot COMe$, has m. p. 93°, b. p. 259—260°/9 mm ; it gives an *oxime*, m. p. 210°. Its constitution is established by the production of dinitrodiphenylmethane-4 : 4′-dicarboxylic acid when it is treated with a mixture of fuming nitric and sulphuric acids, and by the formation of benzophenone-4 : 4′-dicarboxylic acid when it is oxidised with sodium hypobromite. *Acetyldiphenyl-*

methane, $CH_2Ph\cdot C_6H_4\cdot COMe$, m. p. 39°, b. p. 197—198°/9 mm., forms an *oxime*, m. p. 99·5°. On nitration, it gives *nitroacetyldiphenylmethane*, $C_{15}H_{13}O_3N$, which forms needles, m. p. 91·5°, and yields an *oxime*, m. p. 162°. Reduction of the nitro-derivative with alcoholic stannous chloride gives *aminoacetyldiphenylmethane*, m. p. 135·5°.

E. H.

Direct Hydrogenation of Aromatic Quinones. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1908, **146**, 457—458).—The authors have applied the method of direct hydrogenation in the presence of finely-divided nickel to the following aromatic quinones, benzoquinone, toluquinone, *p*-xyloquinone, and thymoquinone, with the result that at about 200° the quinone is converted quantitatively into the corresponding quinol. At temperatures between 220° and 250°, the quinol is reduced with the formation of water and the corresponding hydrocarbon and phenol (compare Sabatier and Senderens, Abstr., 1905, i, 333); at lower temperatures, the quinol is reduced, yielding the corresponding diol of the *cyclo*hexane series. M. A. W.

Hydration of *d*-Pinene. Wladimir Smirnoff (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 150—153).—The hydration of *d*-pinene in the presence of sulphuric acid is a catalytic reaction. The *d*-pinene, mixed with an equal volume of alcohol and about 1/10 by volume of dilute acid, is boiled, a *secondary alcohol*, $C_{10}H_{16},H_2O$, b. p. 93—95°/10 mm., being thus obtained, D^{15}_{15} 0·9216, $D^{18·8}_{4}$ 0·9185, $n^{18·8}_{D}$ 1·4735, $[\alpha]_D$ +44·42°; when oxidised with chromic acid, it yields a *ketone*, b. p. 200—205°, which yields a *semicarbazone*, m. p. 226—228°. Possibly the alcohol is identical with the one obtained by Aschan (Abstr., 1907, i, 630) and with the alcohol obtained from *d*-pinene by the action of dilute nitric acid. In addition to the secondary alcohol, a mixture of hydrocarbons was also obtained, b. p. 148—190°/760 mm. and α + 15° to + 31° (100 mm.).

It is considered that *d*-pinene, b. p. 155—157° and α + 27·4° (100 mm.), which was the substance hydrated, is a mixture of pinene with pinolene or some other unknown hydrocarbon, or undergoes isomeric change into pinolene. Z. K.

Sesquiterpene Occurring together with Cadinene in "Oleum Cadinum." Nicolaus Lepeschkin (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 126—133. Compare Wallach, Abstr., 1887, 595).—In the extraction of cadinene from oleum cadinum, but little of this hydrocarbon is obtained, although a great deal of hydrogen chloride is absorbed, and the object of the research was to discover whether this was not due to the presence of some other hydrocarbon. When the oil remaining after the removal of cadinene from oleum cadinum is distilled at low pressure, a new *sesquiterpene*, $C_{15}H_{24}$, b. p. 262—264°/760 mm., is isolated, together with a mixture of oxidation products of this hydrocarbon of higher b. p. The sesquiterpene has D^{20}_{4} 0·9204, D^{20}_{20} 0·9221, n^{20}_{D} 1·5152, $[\alpha]_D$ 14·12°, and differs entirely from cadinene in chemical properties. It absorbs bromine rapidly with evolution of hydrogen bromide, and does not yield crystalline products with the halogen acid, or give the characteristic colour reactions given by cadinene. With hydrogen iodide at 200° it yields an isomeric *sesquiterpene*, b. p. 250—258°/760 mm., D_4^{20} 0·8946, n_D^{20} 1·4972, either identical or closely related to humulene (Chapman, Trans., 1895, **67**, 54). It is possible that the sesquiterpene occurring together with cadinene in oleum cadinum is identical with that occurring in oil of cubebs.

Z. K.

Constituents of Essential Oils. Composition of Ayapana Oil. Friedrich W. Semmler (*Ber*, 1908, **41**, 509—512).—Ayapana oil, obtained from *Eupatorium triplinerve*, yields on distillation a main fraction, b. p. 116—119°/12 mm., representing 80% of the total, which by redistillation over sodium yields a liquid, b. p. 118°/12 mm., D^{20} 0·9671, n_D 1·51066. This liquid, in spite of the constancy of the b. p., is not an individual substance, for, after being treated with potassium permanganate in cold acetone solution, the recovered liquid has b. p. 118°/12 mm., D^{20} 0·9913, n_D 1·51339, and $\alpha_D \pm 0°$; the other constituent is probably a sesquiterpene. The main portion consists of *thymoquinol dimethyl ether*, $C_{12}H_{18}O_2$, which by treatment with hydriodic acid and red phosphorus at 90° is converted into the *methyl ether* (or a mixture of the isomeric methyl ethers), b. p. 117—130°/12 mm., D^{20} 1·0111, n_D 1·5188, and thymoquinol, $C_{10}H_{14}O_2$, m. p. 143°, the identity of which was proved by oxidation to thymoquinone, m. p. 48°.

C. S.

Essential Oil of Tetranthera polyantha var. citrata. Eugène Charabot and G. Laloue (*Compt. rend.*, 1908, **146**, 349—350; *Bull. Soc. chim.*, 1908, [iv], **3**, 383—388. Compare Schimmel & Co., Abstr., 1905, i, 538).—The oils from the bark, leaves, and fruits have respectively: $\alpha_D + 20°30'$, $-12°30'$, and $+12°44'$ (100 mm. tube); D^{15} 0·8673, 0·9013, and 0·8872. They respectively contain: citral, 8%, citronellal, 20%, an alcohol (geraniol?), 56·5%, ethers, 2·4%; citral, 6%, cineol, 21·2%, an alcohol (geraniol?), 31·3%; citral, 64%, an alcohol (geraniol?), 19·4%, ethers, 2%.

G. B.

Phosphorus, an Essential Constituent of Chlorophyll. Julius Stoklasa, V. Brdlik, and J. Just (*Ber. Deut. bot. Ges.*, 1908, **26***a*, 69—78).—Polemical against Willstätter (Abstr., 1907, i, 71), who found no phosphorus in chlorophyll, or at most traces. The authors have prepared specimens of pure chlorophyll with as much as 3·37% P. The phosphorus content of maple leaves reaches a maximum in July and then falls off, so that only traces are present in October, and at any given time yellow leaves (with little or no chlorophyll) contain much less phosphorus than green leaves of the same plant.

The question is of interest in connexion with the authors' view that chlorophyll is a lecithin-like substance. They have lately shown that choline and glycerophosphoric acids are among its decomposition products.

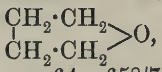
G. B.

Pigment of Yellow Autumn Leaves. M. Tsvett (*Ber. Deut. bot. Ges.*, 1908, **26***a*, 94—101).—The yellow leaves do not contain chlorophyll, but instead a new pigment, which in Kraus' process of separation behaves like carotin, but resembles xanthophyll in that it is wholly adsorbed by calcium carbonate from its solution in light petroleum; it is probably a decomposition product of one of these pigments, or of both. The yellow colouring matter, which is dissolved by boiling the leaves with water, is an artificial product, not concerned in the pigmentation of the living leaf. G. B.

Artificial Melanins, and the Natural Melanin of the Cockchafer. Tomatoro Ishizaka (*Arch. exp. Path. Pharm.*, 1908, **58**, 198—206).—The melanins were prepared from proteins by the following method. The protein was heated for several hours with hydrochloric acid (10%). The dark-coloured liquid was then neutralised with sodium hydroxide and evaporated on a water-bath. Copper acetate was added, and the melanins thereby precipitated. The washed precipitate was dissolved in ammonia; a small amount remained undissolved. This was treated with potassium hydroxide solution on the water-bath; the filtrate from this was added to the ammoniacal solution and the whole made acid with acetic acid and warmed on the water-bath. The melanin was thereby precipitated, and was purified by re-solution in alkali and re-precipitation by acid. Melanins were prepared from gelatin, feathers, sponge, artolin, and nucleic acid. The amount of melanin formed depends on the quantity of sulphur and iodine in the original protein; the larger the amount of these elements present the greater the yield of melanins.

The melanin from cockchafers was extracted with 20% sodium chloride solution containing a little potassium acetate, slightly acidified with acetic acid; from the solution thus obtained, it was precipitated by copper chloride; the free melanin was obtained from this precipitate by a method similar to that described above for the preparation of the protein melanins from their copper compounds. S. B. S.

Hydrogenation of Furan. A. Bourguignon (*Bull. Soc. chim. Belg.*, 1908, **22**, 87—93. Compare Padoa and Ponti, Abstr., 1907, i, 146).—When furan is hydrogenated at 170° by Sabatier and Senderens' method, the principal product consists of *tetrahydrofuran*,

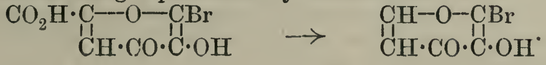


$$\begin{matrix}CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2\end{matrix}\!\!>O,$$

a colourless, mobile liquid, b. p. 64—65°/760 mm., D_4^{21} 0.888 ± 0.002, n_D^{21} 1·40762, having a penetrating odour and a burning, slightly bitter taste, together with a small quantity of *n*-butyl alcohol. Analysis of the gases produced indicates the presence of saturated hydrocarbons, perhaps propane, or a mixture of butane and ethane. Tetrahydrofuran is attacked by bromine, giving a *compound* in the form of a viscous liquid, b. p. 78°/15 mm., which from a bromine estimation appears to be αδ-dibromobutane, $C_2H_4(CH_2Br)_2$.

The conclusion is drawn that the furan nucleus is less stable than that of benzene, which is not ruptured on hydrogenation at 170°. E. H.

Constitution of Halogenated Compounds of 3-Hydroxy-γ-pyrone [Pyromeconic Acid]. I. Compagno (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 73—81).—The distillation of bromocomenic acid (compare Peratoner and Castellana, Abstr., 1905, i, 806) yields a bromopyromeconic acid identical with that obtained by the action of bromine on 3-hydroxy-γ-pyrone (compare Brown, *Annalen*, 1845, **92**, 321), the action being represented by the scheme :



$$\begin{array}{l} CO_2H\cdot C{-}O{-}CBr \\ \qquad\quad CH\cdot CO\cdot C\cdot OH \end{array} \longrightarrow \begin{array}{l} CH{-}O{-}CBr \\ CH\cdot CO\cdot C\cdot OH \end{array}.$$

T. H. P.

Compounds of Dimethylpyrone and Tribromoacetic Acid. Wladimir A. Plotnikoff (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 64—70. Compare Abstr., 1905, i, 77).—The experiments described confirm the existence of compounds of the type RD_2 (where R = a monobasic acid, and D = dimethylpyrone). Thus, by the action of dimethylpyrone on tribromoacetic acid in chloroform or ethereal solution, three crystalline compounds are formed : $CBr_3\cdot CO_2H,C_7H_8O_2$; $2CBr_3\cdot CO_2H,C_7H_8O_2$, and $CBr_3\cdot CO_2H,2C_7H_8O_2$, which decompose at 60° without melting. Physically and chemically the compounds are similar in all respects to true salts. The types and structural formulæ of the compounds dimethylpyrone should form with mono- and di-basic acids are discussed.

Z. K.

Atropine. Richard Wolffenstein and Leonard Mamlock (*Ber.*, 1908, **41**, 723—732).—Ladenburg, in 1883, showed that tropine and tropic acid could be condensed to atropine. Attempts now made to condense tropic acid chloride in a similar manner gave rise only to the formation of tropide from two molecules of the chloride. The chloride of β-chlorohydratropic acid condenses readily with tropine, but attempts to replace the chlorine atom in the β-chlorohydratropyltropine so formed by hydroxyl led only to the formation of *apo*atropine. Acetyltropic acid condenses to acetylatropine, of which the hydrochloride, when left to itself in water, loses the acetyl group, forming atropine.

The *chloride* is obtained from tropic acid by means of thionyl chloride as a yellow oil, which decomposed when distilled. The chloride of β-chlorohydratropic acid is also best prepared by means of thionyl chloride; it condenses with tropine hydrochloride to form the *hydrochloride* of *chlorohydratropyltropeine*, a colourless, crystalline compound, m. p. 167—170°, which forms a crystalline *picrate*, m. p. 204°, and an orange-yellow *platinichloride* (decomp. 60°). When treated with sodium carbonate, this hydrochloride yields the free base as an oil, which, when its ethereal solution is heated, gives rise to a colourless, crystalline salt, *apo*atropine hydrochloride. *Bromohydratropyltropeine hydrobromide* is a snow-white, crystalline mass, m. p. 180°. When evaporated with a few drops of nitric acid and the residue moistened with alcoholic potassium hydroxide, it gives, like the chloro-compound and atropine itself, a violet coloration. Attempts to obtain the free base resulted in the formation of *apo*atropine hydrobromide. Acetyltropic acid was obtained as a yellow, viscid oil, solidifying to a colourless, crystalline mass, m. p. 88—90° (Hesse, Abstr., 1901, i, 713, gives

80°). Thionyl chloride converts this into the *chloride*, which condenses with tropine hydrochloride to *acetylatropine hydrochloride*, a yellow, viscid mass. This is converted readily into atropine on leaving the strongly acid aqueous solution with excess of an alkaline hydroxide.

Physiologically, the chloro- and bromo-hydratropyltropeines behave very much as atropine does, showing that the alcoholic hydroxyl in the aromatic acid radicle in tropeine is replaceable by halogen without affecting the mydriatic action. E. F. A.

Halogen-substituted Tropeines. Richard Wolffenstein and Johannes Rolle (*Ber.*, 1908, **41**, 733—740).—Reactions analogous to the conversion of β-chlorohydratropyltropeine into *apo*atropine have been studied in more simple cases, in which the α, β, and γ halogen derivatives of propionic and *n*-butyric acids were substituted for phenylchloropropionic acid (chlorohydratropic acid). The reaction is a general one, but the readiness with which the elimination of the hydrogen halide is effected is markedly influenced by the position of the halogen. The β-position particularly favours the change, whilst the α and γ positions are less favourable.

α-Chloropropionyl chloride has b. p. 107—110°, and forms a p-*toluidide*, m. p. 108°. *β-Chloropropionyl chloride* has b. p. 144°, and forms a p-*toluidide*, m. p. 121°. *α-Chlorobutyryl*-p-*toluidide* has m. p. 98°; the *β-chlorobutyryl*-p-*toluidide* has m. p. 115°, and the *γ-chlorobutyryl*-p-*toluidide*, m. p. 95°.

These compounds all condense with tropine to form the hydrochlorides of tropeines, which were decomposed with alkaline carbonates, forming an oil which was taken up in benzene solution and rapidly passed into the crystalline, unsaturated tropeine.

α-Chloropropionyltropeine forms an *aurichloride*, crystallising in yellow, glistening plates, m. p. 131°, and a *picrate*, yellow, transparent needles, m. p. 211° (decomp.). *Acryltropeine* forms a crystalline *picrate*, m. p. 198°, and reacts with bromine giving *αβ-dibromopropionyltropeine*, of which the sparingly soluble picrate has m. p. 185°.

β-Chloropropionyltropeine forms a *picrate*, m. p. 222°, a *platinichloride*, m. p. 205, an *aurichloride*, m. p. 135°, and yields the above acryltropeine with greater ease than the β-compound.

α-Chlorobutyryltropeine yields a *picrate*, m. p. 209°, an *aurichloride*, m. p. 125°, and a *platinichloride*, m. p. 212°. *Crotonyltropeine* gives a *picrate*, crystallising in yellow plates, m. p. 190° (decomp.), and an *αβ-dibromobutyryltropeine*.

β-Chlorobutyryltropeine forms a *picrate*, m. p. 216°, an *aurichloride*, m. p. 137° and a *platinichloride*, sparingly soluble needles from alcohol, m. p. 210—212°, and gives the above crotonyltropeine.

γ-Chlorobutyryltropeine forms a *platinichloride*, m. p. 208°, and yields *vinylacetyltropeine* after remaining for thirty days in benzene solution; the *platinichloride* has m. p. 204°.

The acid chlorides described also condense with other alkamines, such as lupinine, and, in particular, dimethylaminomethyldiethylcarbinol. These alkamine-esters show a similar intramolecular elimination of hydrogen chloride. E. F. A.

Pseudomorphism of Organic Persulphates. Richard Wolffenstein and A. Wolff (*Ber.*, 1908, **41**, 717—723).—The persulphates of the cinchonine alkaloids show a new form of pseudomorphism in that, when heated, an intramolecular rearrangement takes place without any change in the atomic composition or external crystalline form. When acid quinine persulphate is heated slowly in an air-bath for eight days, during which time the temperature is slowly allowed to rise from 80° to 120°, the crystals become at first yellow, then reddish-yellow, and finally ruby-red, whilst retaining their transparent appearance and characteristic crystalline form. There is no appreciable change in weight. The substance, formerly sparingly soluble, now dissolves easily in water, but under no condition could it be obtained again in the same crystalline form from this solution. The oxidising action of the persulphate has disappeared. Whereas crystals of quinine persulphate are doubly refractive and anisotropic, those of the heated salt are only singly refractive and *iso*tropic. The action of light on the persulphate slowly brings about a similar change.

During heating, the sulpho-group reacts to sulphonate the quinine molecule. Sulphur is eliminated, however, by heating the product in aqueous solution at 120° under pressure, and a *compound*, $C_{20}H_{24}O_3N_2$, m. p. 113—115°, is formed, which differs from quinine in being sparingly soluble in ether.

Acid cinchonine persulphate undergoes a similar pseudomorphism when heated for three to four days at 60—80°; the product is partly sulphonated, but contains also an oxidation product, forming a bright yellow, amorphous *picrate*, free from sulphur, m. p. 210°. Apparently, during heating, part of the alkaloid remains unchanged, part is more or less oxidised, another part sulphonated, whilst the peroxide oxygen disappears.

Sparingly soluble organic persulphates are best prepared by double decomposition of ammonium persulphate with an acid or neutral salt of the alkaloid. The following have been prepared: *acid quinine persulphate*, $C_{20}H_{24}O_2N_2,H_2S_2O_8$, forms yellowish-white, large, prismatic crystals; the *normal sulphate* gives a mass of small needles. *Acid cinchonine persulphate* crystallises in silky, glistening needles, and the *normal sulphate* in large, prismatic, almost colourless crystals.

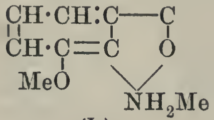
E. F. A.

Alkaloids of the Species of Nigella. Oscar Keller (*Arch. Pharm.*, 1908, **246**, 1—50. Compare Abstr., 1904, i, 768).—An investigation of the constitution of damascenine and of a new alkaloid, methyl damascenine. The seeds of seven species of *Nigella* contain at most traces of alkaloids, but those of *N. damascena* contain 0·5—0·6%, and of *N. aristata*, 0·1%. In the former of these two species, damascenine only is present, but *N. aristata* contains about equal quantities of damascenine and of a new alkaloid, *methyl damascenine*, $C_{10}H_{13}O_3N$, which is the methyl ester of damasceninic acid. This alkaloid forms an oil, which solidifies at low temperatures; unlike damascenine, it does not fluoresce in ethereal solution. The *hydrochloride*, $C_{10}H_{13}O_3N,HCl,H_2O$, forms glistening plates and needles,

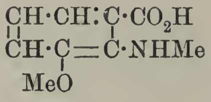
m. p. 121°, and is somewhat less soluble in water than damascenine hydrochloride, which remains in the mother liquor; the *platinichloride*, $(C_{10}H_{13}O_3N)_2,H_2PtCl_6$, needles, m. p. 190—191°, the *methiodide*, $C_{10}H_{13}O_3N,MeI$, broad needles and plates, m. p. 140°, and the *nitroso*-compound, $C_{10}H_{12}O_3N\cdot NO$, m. p. indistinct (60—72°), have been analysed.

By the determination of the position of the carboxyl group in damasceninic acid (an isomeride of damascenine, formed from it by boiling with alkali), this substance is now proved to be 2-*methylamino*-3-*methoxybenzoic acid*, $OMe\cdot C_6H_3(NHMe)\cdot CO_2H$. The proof of this constitution depends on the following substances, which have been obtained from it by the action of hydriodic acid (besides *o*-aminophenol, previously isolated). By the loss of one methyl group there results 2-*methylamino*-3-*hydroxybenzoic acid*, $OH\cdot C_6H_3(NHMe)\cdot CO_2H$, m. p. about 260°. The *hydrochloride*, $C_8H_9O_3N,HCl,\frac{1}{2}H_2O$, melts at 214—215°, and yields, on reduction with sodium amalgam, methylamine and *m*-hydroxybenzoic acid. From the filtrate of the above acid, methyl-*o*-anisidine, $MeO\cdot C_6H_4\cdot NHMe$, was obtained by steam distillation, and there remained in solution 2-*amino*-3-*hydroxybenzoic acid*, $HO\cdot C_6H_3(NH_2)\cdot CO_2H$, glistening leaflets, m. p. 164°. The *hydrochloride*, $C_7H_7O_3N,HCl$, forms granular crystals, m. p. 198—200°. This acid was only obtained in minute quantity, and differs from the three other possible isomerides containing the amino- and hydroxy-groups in the ortho-position to each other, all of which are known.

Since damascenine (I) is devoid of acid properties, but is readily converted into the isomeric damasceninic acid (II), a betaine-like constitution is suggested for it. Methyl damascenine has the formula III:

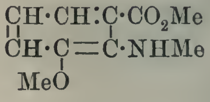


(I.)



$$\begin{array}{l} CH\cdot CH:C\cdot CO_2H \\ CH\cdot C=C\cdot NHMe \\ \quad MeO \end{array}$$

(II.)



$$\begin{array}{l} CH\cdot CH:C\cdot CO_2Me \\ CH\cdot C=C\cdot NHMe \\ \quad MeO \end{array}$$

(III.)

Methyl damascenine is readily formed from the silver salt of damasceninic acid and methyl iodide, and yields, on heating with water or dilute alkali, both the original acid and damascenine.

The synthesis of both alkaloids depends therefore on that of damasceninic acid. With this end in view, the introduction of a methoxy-group into methylanthranilic acid was attempted. By nitration, 3-nitro-2-methylaminobenzoic acid, m. p. 146°, and 5-nitro-2-methylaminobenzoic acid are simultaneously formed. The *hydrochlorides*, $NHMe\cdot C_6H_3(CO_2H)\cdot NH_2,HCl$, of the corresponding aminomethylaminobenzoic acids melt at 205° and 214° respectively. After diazotisation, the direct introduction of a methoxy-group was found to be impossible; neither could a hydroxyl group be introduced, for both acids yielded very stable, red, crystalline substances with feeble acidic, and very feeble basic, properties, m. p. 266° and 268° respectively. These substances both have the composition of a *methylaziminobenzoic acid*, $C_8H_7O_2N_3$, and are presumably internal anhydrides of the diazonium group with either the carboxyl or the methylamino-group. By Sandmeyer's reaction, *5-chloro-2-methylaminobenzoic acid*,

$$NHMe\cdot C_6H_3Cl\cdot CO_2H,$$

needles, m. p. 173°, was obtained. Of the corresponding 3-chloro-acid, m. p. 143°, mere traces, insufficient for analysis, were obtained.

An attempt to synthesise an isomeride of damasceninic acid led to production (from 3-nitrosalicylic acid) of three substances having the composition $C_8H_7O_5N$, namely, *methyl 3-nitrosalicylate*, needles, m. p. 93°, obtained by esterification with hydrogen chloride, and two *acids*, both crystallising in needles and melting at 110° and 125° respectively. These acids were obtained from the dipotassium salt of 3-nitrosalicylic acid and methyl sulphate, and may hence be regarded as nitromethoxybenzoic acids; their isomerism remains unexplained.

G. B.

Preparation of Narcotine Derivatives. KNOLL & Co. (D.R.-P. 188054 and 188055. Compare Abstr., 1907, i, 235).—Although it was formerly supposed that narcotine was not affected by acetic anhydride, it has now been ascertained that a mixture of this substance and sulphuric acid, which has been heated until it no longer gives the reaction for sulphuric acid, will effect the acetylation of the alkaloid when the reagents are heated together at 80°.

Acetylnarcotine, $C_{22}H_{22}O_7NAc$, m. p. 159—161°, is soluble in alcohol or acids, but does not dissolve in aqueous alkalis. When narcotine is treated in the cold with a mixture of sulphuric acid and acetic anhydride which has not been heated above 30°, it undergoes sulphonation.

Narcotinesulphonic acid, $C_{22}H_{22}O_7N\cdot SO_3H$, is precipitated as a white powder from the sulphonation mixture by the addition of dry ether.

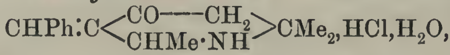
G. T. M.

1-*p*-Hydroxybenzylpiperidine. WILHELM KÖNIGS and KARL BERNHART (*Ber.*, 1908, **41**, 499—500).—1-*Anisylpiperidine*, prepared by acting on piperidine with anisyl chloride, is a colourless oil, b. p. about 283°/712 mm.; the *picrate* has m. p. about 163°. Boiling concentrated hydrobromic acid converts 1-anisylpiperidine into 1-p-*hydroxybenzylpiperidine hydrobromide*, $C_{12}H_{17}ON,HBr$, obtained as a colourless, crystalline powder, m. p. about 216°; the free *base* crystallises in prisms, m. p. 140°. The hydrobromide is decomposed by bromine water with the formation of tribromophenol and piperidine in quantities represented by the equation: $C_{12}H_{17}ON + H_2O + 3Br_2 = C_6H_2Br_3\cdot OH + C_5H_{11}N + H\cdot CHO + 3HBr$, whilst only traces of formaldehyde were detected. The base is not decomposed by dry bromine, but is converted into a *dibromo*-derivative, $C_{12}H_{15}ONBr_2$, crystallising in small, yellow prisms, m. p. about 182° (decomp.); the *hydrobromide* crystallises in colourless prisms, m. p. about 223° (decomp.).

W. H. G.

Condensation of Benzaldehyde with Cyclic Acetone Bases. HERMANN PAULY and O. K. RICHTER (*Ber.*, 1908, 41, 464—469).—A study of the influence of methyl groups on condensation reactions.

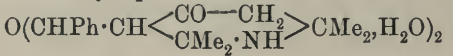
Pauly (Abstr., 1899, i, 228) observed that, whilst vinyldiacetonamine reacts normally with mercaptans, forming dimercaptols, the accumulation of methyl groups in triacetonamine influences the course of the reaction in such a manner that the acetone base reacts with only 1 mol. of mercaptan. It is now found that in the condensation of acetone bases with benzaldehyde, the retarding influence of the methyl groups is apparent even in the case of vinyldiacetonamine. In presence of hydrogen chloride in glacial acetic acid solution at the ordinary temperature, vinyldiacetonamine and triacetonamine react with benzaldehyde only after some weeks, forming a monobenzylidene derivative and an aldol-like product respectively. In aqueous alcoholic sodium hydroxide or methoxide solution, vinyldiacetonamine undergoes only partial condensation with benzaldehyde, forming a *product*, $C_{25}H_{25}O_2N$ (?), crystallising in needles, m. p. 162°, whilst triacetonamine remains unchanged. Hence condensation with benzaldehyde is not an unfailing test for the presence of the group $\cdot CH_2\cdot CO\cdot CH_2\cdot$.

Benzylidenevinyldiacetonamine is isolated in the form of its *hydrochloride*,  $CHPh{:}C<\begin{array}{c}CO\text{---}CH_2\\ CHMe\cdot NH\end{array}>CMe_2,HCl,H_2O$, which crystallises in yellowish-white needles, m. p. 204°, and gives a red coloration with sulphuric acid.

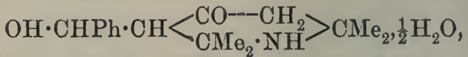
The *condensation product* of benzaldehyde and triacetonamine,

$$C_{16}H_{22}ONCl,HCl,$$

crystallises in white needles, m. p. 174°, is decomposed into its generators when gently heated with sodium hydroxide, and is converted by aqueous sodium carbonate into a *product*,

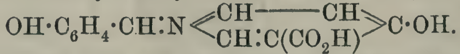


$$O(CHPh\cdot CH<\begin{array}{c}CO\text{---}CH_2\\ CMe_2\cdot NH\end{array}>CMe_2,H_2O)_2 \text{ or}$$



$$OH\cdot CHPh\cdot CH<\begin{array}{c}CO\text{---}CH_2\\ CMe_2\cdot NH\end{array}>CMe_2,\tfrac{1}{2}H_2O,$$

which crystallises in white needles, m. p. 175°, decomposes slowly at 105—125°, and yields benzaldehyde and triacetonamine when boiled with alcohol; the *hydrochloride*, m. p. about 150°. G. Y.

Condensation of Aminohydroxy-acids with Aromatic Aldehydes. I. Ernesto Puxeddu (*Gazzetta*, 1908, **38**, i, 8—18).—After discussing previous work on this subject, the author describes his attempts to obtain condensation products of 5-aminosalicylic, 5-amino-*m*-cresotic, and 5-amino-*o*-cresotic acids with benzaldehyde, *m*-nitrobenzaldehyde, salicylaldehyde, cinnamaldehyde, and piperonaldehyde. The aldehyde was dissolved in a small quantity of cold alcohol, and was then well mixed for some hours or days with an equal weight of the powdered aminohydroxy-acid. The velocity with which the condensation proceeds varies widely with the nature of the reacting compounds. The condensation products are all of the same type, that formed between salicylaldehyde and 5-aminosalicylic acid having the constitution  $OH\cdot C_6H_4\cdot CH{:}N<\begin{array}{c}CH\text{------}CH\\ CH{:}C(CO_2H)\end{array}>C\cdot OH$.

5-Aminosalicylic acid and *m*-nitrobenzaldehyde yield the *compound*,

$C_{14}H_{10}O_5N_2$, crystallising from alcohol in yellow, prismatic needles, m. p. 245° (decomp.).

5-Aminosalicylic acid and cinnamaldehyde give the *compound*, $C_{16}H_{13}O_4N$, which crystallises from alcohol in red, prismatic needles, m. p. 130° (decomp.).

5-Aminosalicylic acid and piperonaldehyde yield the *compound*, $C_{15}H_{11}O_5N$, m. p. 250° (decomp.).

5-Amino-*o*-cresotic acid and *m*-nitrobenzaldehyde give the *compound*, $C_{15}H_{12}O_5N_2$, crystallising from alcohol in minute, faintly-yellow prisms, m. p. 250° (decomp.).

5-Amino-*o*-cresotic acid and salicylaldehyde yield the *compound*, $C_{15}H_{13}O_4N$, which crystallises from alcohol in small, mamillary masses, m. p. 230° (decomp.).

5-Amino-*o*-cresotic acid and cinnamaldehyde give the *compound*, $C_{17}H_{15}O_3N$, crystallising from alcohol in deep, wine-red, acicular prisms, m. p. 175° and onwards (decomp.).

5-Amino-*m*-cresotic acid and salicylaldehyde yield the *compound*, $C_{15}H_{13}O_4N$, which crystallises from alcohol in brownish-green, dichroic prisms, m. p. 223° (decomp.).

5-Amino-*m*-cresotic acid and cinnamaldehyde give the *compound*, $C_{17}H_{15}O_3N$, crystallising from alcohol in prismatic scales, m. p. 174° (decomp).

All these compounds are acid in character, dissolving in solutions of alkali hydroxide or carbonate; they give colorations with ferric chloride.

No condensation products were obtained with: 5-aminosalicylic acid and benzaldehyde; 5-amino-*o*-cresotic acid and benzaldehyde; 5-amino-*o*-cresotic acid and piperonaldehyde; 5-amino-*m*-cresotic acid and benzaldehyde; 5-amino-*m*-cresotic acid and *m*-nitrobenzaldehyde; 5-amino-*m*-cresotic acid and piperonaldehyde. T. H. P.

Preparation of Normal Salts of *o*-Hydroxyquinoline with Polybasic Acids. FRANZ FRITZSCHE & Co. (D.R.-P. 187943).—The normal salts of *o*-hydroxyquinoline with the polybasic acids readily dissociate in solution into acid salts and free *o*-hydroxyquinoline, which is very volatile either alone or in the presence of solvents. On this account, these salts must be prepared directly by precipitation, and not by concentration of their solutions.

o-*Hydroxyquinoline sulphate*, $(C_9H_7ON)_2,H_2SO_4$, a yellow, crystalline powder, m. p. 177·5°, obtained by mixing its components in 96% alcohol, is readily soluble in water and quite insoluble in ether. o-*Hydroxyquinoline phosphate*, $(C_9H_7ON)_3,H_3PO_4$, yellow, crystalline powder, m. p. 184°, o-*hydroxyquinoline succinate*,

$$(C_9H_7ON)_2,C_4H_6O_4,$$

m. p. 138°, o-*hydroxyquinoline* o-*hydroxyquinolinesulphonate*,

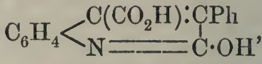
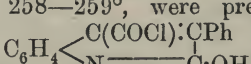
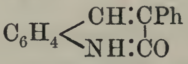
$$C_9H_7ON,C_9H_6ON\cdot SO_3H,$$

satiny needles, m. p. 300°, and o-*hydroxyquinoline salicylate*,

$$(C_9H_7ON)_2,OH\cdot C_6H_4\cdot CO_2H,$$

yellow leaflets, m. p. 113°, are similarly prepared. These salts are all readily soluble in water, giving a neutral solution. G. T. M.

Derivatives of 3-Phenylquinoline. H. HÜBNER (*Ber.*, 1908, 41, 482—487).—A continuation of the investigation on 3-phenylcinchonic acid (Abstr., 1906, i, 383). The hydrazide of 3-phenylcinchonic acid (*loc. cit.*) condenses with benzaldehyde, yielding a *condensation product*, $C_{23}H_{17}ON_3$, m. p. 232°, and with acetone, yielding a *condensation product*, $C_{19}H_{17}ON_3$, m. p. 191°. 3-Phenylquinoline is formed on heating 3-phenylcinchonic acid about 15° above its melting point; it crystallises in large, transparent plates, m. p. 52°; Friedländer and Gohring state that it is an oil (Abstr., 1883, 1148). The *picrate*, $C_{15}H_{11}N,C_6H_3O_7N_3$, forms yellow crystals, m. p. 205°; the *ethiodide* has m. p. 228°; the *methiodide*, $C_{16}H_{14}NI$, crystallises in small, yellow needles, m. p. 224°, and it is converted by the method of Königs and Meimberg (Abstr., 1895, i, 430) into 3-*phenyl*-1-*methyl*-2-*quinoline*, $C_{16}H_{13}ON$, m. p. 138°.

2-*Hydroxy*-3-*phenylcinchonic acid*,  $C_6H_4<\begin{array}{l}C(CO_2H){:}CPh\\ N{=\!=\!=\!=\!=}C\cdot OH\end{array}$, prepared by heating isatin with phenylacetic anhydride at 180°, has m. p. 291°; the *silver* salt, $C_{16}H_{10}O_3NAg,H_2O$, and crystalline *methyl* ester, $C_{17}H_{13}O_3N$, m. p. 258—259°, were prepared. 2-*Hydroxy*-3-*phenylcinchonyl chloride*,  $C_6H_4<\begin{array}{l}C(COCl){:}CPh\\ N{=\!=\!=\!=\!=}C\cdot OH\end{array}$, m. p. 234°, obtained by heating the acid with thionyl chloride in a a sealed tube at 100°, is converted by ammonia into the *amide*, $C_{16}H_{12}O_2N_2$, m. p. 296—298°, by hydrazine into the *hydrazide*, $C_{16}H_{13}O_2N_3$, m. p. 298°, and by aniline into the *anilide*, $C_{22}H_{16}O_2N_2$, m. p. 313°. 2-Hydroxy-3-phenylcinchonic acid decomposes at 320—330° into carbon dioxide and 3-phenylcarbostyril, which, since it is almost insoluble in alkalis, probably has the formula  $C_6H_4<\begin{array}{l}CH{:}CPh\\ NH{:}CO\end{array}$ (compare Bischler and Lang, Abstr., 1895, i, 250). 2-*Chloro*-3-*phenylcinchonyl chloride*, $C_{16}H_9ONCl_2$, m. p. 163°, is formed on heating 2-hydroxy-3-phenylcinchonic acid with thionyl chloride under pressure at 180°; it is converted by ammonia into the *amide*, $C_{16}H_{11}ON_2Cl$, m. p. 302°, and, when boiled with an aqueous solution of sodium hydrogen carbonate, yields 2-*chloro*-3-*phenylcinchonic acid*, $C_{16}H_{10}O_2NCl$, m. p. 226°; the *silver* salt, $C_{16}H_9O_2NAg$, was prepared and analysed. W. H. G.

Preparation of Diphenylamine Derivatives. IRMA GOLDBERG (D.R.-P. 187870. Compare Abstr., 1906, i, 953).—Diphenylamine derivatives are obtained in good yield when aromatic amines are heated with bromobenzene in the presence of cuprous iodide.

Diphenylamine itself is formed on boiling for fifteen hours a mixture of aniline, cuprous iodide, potassium carbonate, and excess of bromobenzene, and may also be produced from acetanilide, bromobenzene, cuprous iodide, and potassium carbonate when these are heated together in nitrobenzene. The replacement of acetanilide by *p*-nitroaniline in the foregoing condensation leads to the production of *p*-nitrodiphenylamine; the addition of a small amount of iodobenzene to the mixture facilitates the reaction.

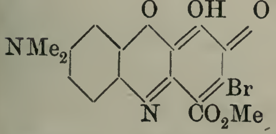
o- and *m*-Nitrodiphenylamines can be produced in a similar manner from *o*- and *m*-nitroanilines. Phenylanthranilic acid is obtained by boiling in amyl-alcoholic solution a mixture of anthranilic acid, bromobenzene, potassium carbonate, and cuprous iodide.

It has been stated previously that aromatic amines and bromobenzene do not interact to furnish diphenylamine derivatives, but this want of success is due to the employment of copper powder or cupric chloride as catalyst. In the presence of cuprous iodide, the condensations are readily effected. G. T. M.

Formation of Dyes in Ultra-violet Light. Carl Schall (*J. pr. Chem.*, 1908, [ii], **77**, 262—266. Compare Vignon, Abstr., 1888, 1012; 1889, 1099; Gabutti, Abstr., 1902, i, 312).—The behaviour of paper soaked in a molecular, aqueous solution of *p*-phenylenediamine and nitric acid (this vol., ii, 139) results from the formation of the *mononitrate*, $C_6H_4(NH_2)_2,HNO_3$, which crystallises in transparent needles, and becomes greyish-violet when dried or instantaneously green to greenish-blue on exposure to ultra-violet rays. Paper soaked in a solution of the salt and dried, becomes blue when exposed to ultra-violet light. The greenish-blue substance, when shaken with ether and very dilute sodium hydroxide, forms a brownish-red ethereal solution. The nature and mode of formation of the coloured product is discussed.

p-*Phenylenediamine dinitrate*, $C_6H_4(NH_2)_2,2HNO_3$, forms colourless crystals, and on exposure to ultra-violet light when anhydrous decomposes, becoming yellow and finally dark brown, but, if moist, gives a blue coloration in consequence of hydrolysis to the mononitrate. G. Y.

Pruneanilide. Eugène Grandmougin and Ernst Bodmer (*Ber.*, 1908, **41**, 604—611. Compare Abstr., 1907, i, 355).—Pruneanilide was regarded by Nietzki and Bossi (Abstr., 1893, i, 44) as an additive compound of prune (1 mol.) and aniline (1 mol.), because hydrogen was not evolved in the reaction. Hydrogen is produced, however, as in the equation $C_{16}H_{14}O_5N_2 + NH_2Ph = C_{16}H_{13}O_5N_2{\cdot}NHPh + H_2$, but is not evolved, being utilised in reducing unchanged prune to the leuco-compound, which does not react with aniline. Only one-half of the prune can therefore be converted into the anilide, but the yield is doubled by passing air through the reacting mixture. Pruneanilide, $C_{22}H_{19}O_5N_3$, forms green prisms which are violet in transmitted light; the reddish-violet solution in concentrated sulphuric acid changes by dilution through blue to red. The constitution has been proved in the following way. The action of nitrosodimethylaniline hydrochloride on methyl dibromogallate in methyl-alcoholic solution leads to the formation of bromoprune, which has been obtained impure by Biétrix (Abstr., 1897, i, 289) and must, by its method of formation, have the annexed formula. When bromoprune, dissolved in alcohol containing a few drops of hydrochloric acid, is heated with



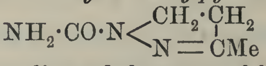
aniline, pruneanilide is obtained by the replacement of the halogen by the anilino-group.

Pruneanilide is hydrolysed by acids, aniline being eliminated and *hydroxyprune*, $C_{16}H_{14}O_6N_2$, formed, in which the presence of two hydroxyl groups is proved by the action of benzenesulphonyl chloride, whereby the *ester*, $C_{28}H_{22}O_{10}N_2S_2$, is obtained, which separates from ethyl acetate in green needles, is sparingly soluble in dilute acids, insoluble in alkalis, and forms solutions with a strong red fluorescence.

Coelestin blue B (Correin RR), the amide corresponding with prune, and aniline also form an *anilide*, $C_{23}H_{22}O_4N_4$, of analogous constitution, the yield of which is increased in a current of air. It separates from glacial acetic acid in green crystals, dissolves in concentrated sulphuric acid with a magenta-red colour, and very slightly in dilute alkalis with a violet-blue colour. C. S.

Action of Nitrogen-containing Reagents on the Carbonyl Group of β-Chloroethyl- and Alkyl Vinyl-ketones. M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 272—280).—When β-chloroethyl ketones are treated with the usual reagents for the detection of a carbonyl group, they condense in the normal manner, but the products are unstable and readily lose 1 mol. of hydrogen chloride to form heterocyclic substances. Similar products are formed by the interaction of these reagents with alkyl vinyl ketones.

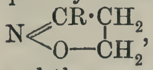
The following substances were obtained by boiling aqueous solutions of sodium acetate, holding in suspension the appropriate β-chloroethyl alkyl ketone semicarbazone, the latter being in each case a colourless, unstable, sparingly soluble substance (compare Scholtz and Kipke, Abstr., 1904, i, 508); 1-*carbamyl-3-methylpyrazoline*,



$$NH_2\cdot CO\cdot N<\begin{matrix}CH_2\cdot CH_2\\ N=CMe\end{matrix},$$

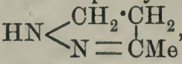
m. p. 167°; the corresponding *ethyl* compound has m. p. 96°, and yields a *picrate*, m. p. 137°; the *propyl* derivative, m. p. 108°, forms large crystals from ether.

The oximes of the β-chloroethyl alkyl ketones cannot be isolated, but, on warming the solutions in which they are formed and subsequently extracting with ether, the corresponding 3-alkyl*iso*oxazolines,



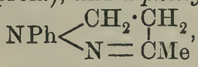
$N<\begin{matrix}CR\cdot CH_2\\ O—CH_2\end{matrix}$, are obtained. 3-*Methyl*iso*oxazoline*, b. p. 60°/15 mm., and the corresponding *ethyl* and *propyl* compounds, b. p. 69°/11 mm. and b. p. 77°/8 mm. respectively, are colourless liquids of unpleasant odour and feebly basic properties; ethyl *iso*oxazoline yields a *platinum derivative*, $2C_5H_9ON,PtCl_4$, m. p. 170°.

With hydrazine and phenylhydrazine, both the β-chloroethyl alkyl ketones and the corresponding alkyl vinyl ketones yield eventually the same 3-alkylpyrazolines and 1-phenyl-3-alkylpyrazolines respectively. 3-*Methylpyrazoline*,



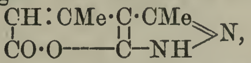
$HN<\begin{matrix}CH_2\cdot CH_2\\ N=CMe\end{matrix}$, b. p. 56°/15 mm., gives a *picrate*, m. p. 153°, and a *phenylcarbamide*, m. p. 109°; 3-*ethylpyrazoline*, b. p. 76°/22 mm., yields a *picrate*, m. p. 117°, and a *phenyl-*

carbamide, m. p. 76°; the *propyl* derivative has b. p. 82°/15 mm., and yields a *picrate*, m. p. 150° (approx.), and a *phenylcarbamide*, m. p. 55°.

1-*Phenyl-3-methylpyrazoline*,  $\mathrm{NPh}\Big\langle\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{N{=}CMe}\end{array}$, m. p. 76—77°, crystallises from ether. The corresponding *ethyl* and *propyl* compounds are liquids, b. p. 155°/9 mm. and b. p. 162°/10 mm. respectively.

T. A. H.

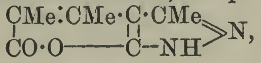
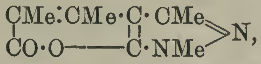
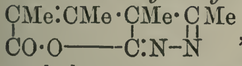
Lactones of the Pyrazole Series. LUDWIG WOLFF and WILHELM SCHREINER (*Ber.*, 1908, 41, 550—558. Compare Abstr., 1905, i, 839).—The azine of ethyl acetoacetate loses alcohol when heated, forming a compound, m. p. 246°, which is also obtained by melting the condensation product of 3-methylpyrazolone and ethyl acetoacetate. This method of preparation and the conversion by means of sodium hydroxide into an acid containing an additional molecule of water suggest the lactone formula

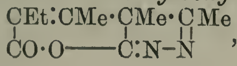


$$\begin{array}{l}\mathrm{CH{:}CMe\cdot C\cdot CMe}\\ \mathrm{CO\cdot O{-}{-}{-}C{-}NH}\end{array}\!\!>\mathrm{N},$$

and further evidence is now adduced in favour of it.

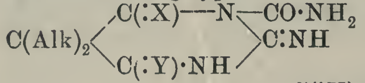
The lactone forms an *acetyl* derivative crystallising in colourless needles, m. p. 184°, and reacts with bromine, forming yellow crystals of the *dibromide*, which are decomposed by moisture, forming the colourless *monobromo*-derivative, m. p. 218° (decomp.). When this is warmed with sodium hydroxide, the lactone ring is broken and the corresponding *brominated acid* formed, m. p. 145° (decomp.).

The *methylated lactone*,  $\begin{array}{l}\mathrm{CMe{:}CMe\cdot C\cdot CMe}\\ \mathrm{CO\cdot O{-}{-}{-}C{-}NH}\end{array}\!\!>\mathrm{N}$, prepared by the condensation of 3-methylpyrazolone with ethyl methylacetoacetate, forms long, colourless needles, m. p. 253°, and is converted by sodium hydroxide into 3-*methylpyrazolone*-4-iso*butylenecarboxylic acid*, m. p. 162° (decomp.). This acid is converted into the lactone on warming with 5% hydrochloric acid or on boiling with water. The *dimethylated lactone*,  $\begin{array}{l}\mathrm{CMe{:}CMe\cdot C\cdot CMe}\\ \mathrm{CO\cdot O{-}{-}{-}C\cdot NMe}\end{array}\!\!>\mathrm{N}$, prepared by heating ethyl methylacetoacetate with 1 : 3-dimethylpyrazolone, crystallises in long needles, m. p. 181°; it is sparingly soluble in cold sodium hydroxide, and is decomposed by this on heating. It is isomeric with the *lactone* of 5-*hydroxy*-3 : 4-*dimethylpyrazole*-4-iso*butylenecarboxylic acid*,  $\begin{array}{l}\mathrm{CMe{:}CMe\cdot CMe\cdot CMe}\\ \mathrm{CO\cdot O{-}{-}{-}C{:}N{-}N}\end{array}$, prepared either by heating the azine of ethyl methylacetoacetate at 200° or by heating 3 : 4-dimethylpyrazolone with ethyl methylacetoacetate, or, finally, by heating dimethylpyrazolone with ethyl acetoacetate, whereby a rearrangement is effected. It crystallises in long, colourless needles, m. p. 181°, and dissolves in warm sodium hydroxide, forming the corresponding *acid*, isolated as *barium* salt, since the acid is very easily reconverted into lactone.

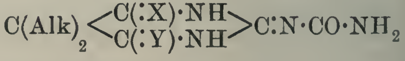
The *lactone* of 5-*hydroxy*-3 : 4-*dimethylpyrazole*-4-iso*amylenecarboxylic acid*,  $\begin{array}{l}\mathrm{CEt{:}CMe\cdot CMe\cdot CMe}\\ \mathrm{CO\cdot O{-}{-}{-}C{:}N{-}N}\end{array}$, prepared from 3 : 4-dimethylpyrazolone and ethyl ethylacetoacetate, crystallises in long, colourless needles, m. p. 132°. By the hydrolysis of ethyl 3-methylpyrazolone-4-*iso*propylenecarboxylate with cold sodium hydroxide, a third 3-*methylpyrazolone*iso*propylenecarboxylic acid* is obtained, isomeric with the two previously described (Abstr., 1905, i, 839). The anhydrous acid melts about 90°, but when containing $2H_2O$, it shows m. p. 135—140°, decomposing thereby to 3-methyl-4-*iso*propylenepyrazolone and carbon dioxide. E. F. A.

Traube's Pyrimidine Synthesis. FRITZ BAUM (*Ber.*, 1908, 41, 532—540. Compare Traube, Abstr., 1901, i, 54; 1904, i, 632; Conrad, 1905, i, 751).—The explanation, that the closing of the ring in the synthesis of a pyrimidine derivative from a cyanoacetic acid is due to the hydrolysis of the nitrile radicle to amide and subsequent withdrawal of the elements of water, is questioned. Cyanoacetyldimethylcarbamide (compare this vol., i, 253) undergoes this change, not only with extraordinary ease in the presence of sodium carbonate or sodium hydrogen carbonate, but also in the presence of disodium hydrogen phosphate, borax, sodium sulphite, or potassium acetate. Cyanoacetylmethylcarbamide undergoes this change less readily, hydrolysis also occurring, and cyanoacetylcarbamide with these reagents does not yield pyrimidines. However, magnesium oxide converts these open-chain methyl carbamides in hot solution into the corresponding ring compounds, and even in the case of the carbamide compound the presence of the cyclic compound can be demonstrated by the nitroso-reaction. Sodium nitrite also has the property of converting the methylcarbamide. The experiments show that the hydrolysis and the closing of the ring are two independent reactions, and the conclusion is drawn that the unsaturated character of the nitrile group is the prime cause of the ring formation. W. R.

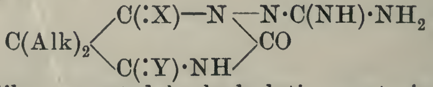
Preparation of 5 : 5-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 187990. Compare Abstr., 1906, i, 538).—Guanylcarbamide reacts in one or other of the forms $NH_2\cdot CO\cdot NH\colon C(NH)\cdot NH_2$ and $NH_2\cdot CO\cdot N\colon C(NH_2)_2$, and, when condensed with alkyl dialkylmalonates and alkyl dialkylcyanoacetates, dialkylmalonyl halides or dialkylmalononitriles furnish substances of the following types:



$$C(Alk)_2\!<\!\begin{matrix}C(:X)-N(CO\cdot NH_2)\\ C(:Y)\cdot NH\end{matrix}\!>\!C\colon NH$$



$$C(Alk)_2\!<\!\begin{matrix}C(:X)\cdot NH\\ C(:Y)\cdot NH\end{matrix}\!>\!C\colon N\cdot CO\cdot NH_2$$

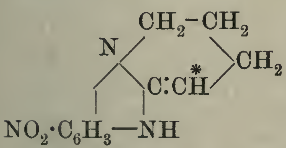


$$C(Alk)_2\!<\!\begin{matrix}C(:X)-N(N\cdot C(NH)\cdot NH_2)\\ C(:Y)\cdot NH\end{matrix}\!>\!CO$$

which are readily converted by hydrolytic agents into 5 : 5-dialkylbarbituric acids.

5 : 5-Diethylbarbituric acid is obtained by hydrolysing at 100° with 50% sulphuric acid the condensation product from guanylcarbamide and ethyl diethylmalonate, ethyl cyanodiethylacetate, or diethylmalononitrile. Oxalic or nitric acid may be also used to effect the hydrolysis. G. T. M.

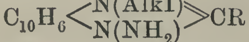
Reduction of Dinitrophenylpiperidine. II. LEOPOLD SPIEGEL and H. KAUFFMANN (*Ber.*, 1908, **41**, 679—685. Compare Spiegel and Utermann, Abstr., 1906, i, 882).—In the reduction of *o*-*p*-dinitropiperidine by Lellmann and Geller's method (Abstr., 1888, 1107), a *base*, $C_{11}H_{11}O_2N_3$, is obtained, insoluble in ether and sodium hydroxide, in addition to the *p*-nitro-*o*-aminopiperidine previously described. It forms almost colourless crystals from benzene, m. p. 219—220°; the *hydrochloride* forms large, stepped crystals. On benzoylation, the base gives a monobenzoyl derivative, soluble in potassium hydroxide, $C_{18}H_{17}O_4N_3$, and crystallising from benzene in slender needles, m. p. 196°. The chief product is a dibenzoyl derivative, $C_{25}H_{19}O_4N_3$, which crystallises in thick, faintly yellowish-green crystals, m. p. 188°. This substance, when heated at 120—130° for eight hours in a sealed tube with hydrochloric acid (D 1·12), yields benzoic acid and a *ketone*, $C_{18}H_{15}O_3N_3$, which crystallises in slender needles, m. p. 178°; the *oxime*, $C_{18}H_{16}O_3N_4$, crystallises in yellow needles, m. p. 226°. The conclusion is arrived at that the base, *benziminoazopiperidine*, has the annexed constitution, the glyoxaline ring being opened during benzoylation, forming 4-*nitro*-2-*benzoylamino*-N-*phenylpiperidone* (compare Bamberger, Abstr., 1893, i, 437). The dibenzoyl compound is supposed to be *dibenzoylnitroiminoazopiperidine*, the hydrogen atom marked with the asterisk is, perhaps, active like the methyl in μ-methylbenziminoazolines (Bamberger, Abstr., 1893, i, 433).



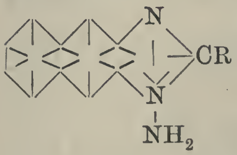
A better method of preparing dinitrophenylpiperidine from chlorodinitrobenzine, piperidine, and sodium ethoxide is described. The yield is 80%.

p-Nitro-*o*-aminophenylpiperidine, on oxidation with Caro's acid, leads to the formation of the base. W. R.

***N*-Aminoheterocyclic Compounds. II. 1-Amino-2-*p*-*iso*propylphenyl-2 : 3-naphthaglyoxaline.** HARTWIG FRANZEN and R. SCHEUERMANN (*J. pr. Chem.*, 1908, [ii], **77**, 193—225. Compare Abstr., 1906, i, 706).—1-Amino-2-*p*-*iso*propylphenyl-2 : 3-naphthaglyoxaline, which is prepared from 2 : 3-naphthylenedihydrazine and *p*-*iso*propylbenzaldehyde in the same manner as 1-amino-2-phenyl-2 : 3-naphthaglyoxaline from the dihydrazine and benzaldehyde (*loc. cit.*), is compared, on the one hand, with *as.*-*sec.*-hydrazines and *N*-aminoheterocyclic compounds, such as piperylhydrazine, which resembles *as.*-*sec.*-hydrazines, and, on the other, with α-acyl-*prim.*-hydrazides. *as.*-*sec.*-Hydrazines undergo the following typical reactions: (1) oxidation to tetrazones by mercuric oxide; (2) ready conversion into secondary amines by the action of nitrous acid; (3) formation of quaternary azonium derivatives with alkyl iodides; (4) condensation with aromatic and (5) aliphatic aldehydes, and (6) with ketones; (7) condensation with pyruvic acid in cold acid solution; (8) reduction of Fehling's solution when heated; (9) formation of semicarbazides with cyanic acid, and (10) of phenylthiosemicarbazides with phenylthiocarbimide, and (11) formation of acyl derivatives with acid anhydrides. Of these eleven reactions, α-acyl-*prim.*-hydrazides undergo all except (1), (3), (5), and (7), but the 1-amino-2 : 3-naphthaglyoxalines undergo only reactions (4), (10), and (11). The formation of derivatives of the type


$$C_{10}H_6<\begin{matrix}N(AlkI)\\N(NH_2)\end{matrix}>CR$$

by the action of alkyl iodides on the 1-amino-2 : 3-naphthaglyoxalines is explained by assuming a centric structure for the latter, in which the nitrogen atom in position 1 being already quinquevalent cannot form additive compounds.



A list is given of the *N*-aminoheterocyclic compounds which have been described in the literature.

1 : 3-*Di*-p-iso*propylbenzylideneamino*-2-p-iso*propylphenyl*-2 : 3-*naphthaglyoxaline*, $C_{10}H_6<\begin{matrix}N(N{:}CH\cdot C_6H_4Pr^{\beta})\\N(N{:}CH\cdot C_6H_4Pr^{\beta})\end{matrix}>CH\cdot C_6H_4Pr^{\beta}$, prepared by boiling 2 : 3-naphthylenedihydrazine with *p-iso*propylbenzaldehyde in alcoholic solution, crystallises from xylene in yellow needles, m. p. 220°, and gives a red coloration with concentrated sulphuric acid. When boiled with concentrated hydrochloric acid and glacial acetic acid, it yields benzaldehyde and the *hydrochloride* of 1-amino-2-*p-iso*propylphenyl-2 : 3-naphthaglyoxaline, $C_{20}H_{19}N_3,HCl$, which crystallises in yellowish-white needles, m. p. 249° (decomp.). The free *base*, $C_{10}H_6<\begin{matrix}\overline{\qquad\quad}N\\N(NH_2)\end{matrix}>C\cdot C_6H_4Pr^{\beta}$, crystallises in dirty white leaflets, m. p. 265°. The *sulphate*, $(C_{20}H_{19}N_3)_2,H_2SO_4$, yellow needles, sinter at 135°, *nitrate*, needles, m. p. 161° (decomp.), *picrate*,

$$C_{20}H_{19}N_3,C_6H_3O_7N_3,$$

greenish-yellow needles, m. p. 223°, and *platinichloride*,

$$(C_{20}H_{19}N_3)_2,H_2PtCl_6,$$

decomp. 240°, are described. The *acetyl* derivative, $C_{20}H_{17}N_2\cdot NHAc$, prepared by boiling the base with acetic anhydride, crystallises in needles, m. p. 248°, and forms a *picrate*, $C_{28}H_{24}O_8N_6$, crystallising in yellow needles, m. p. 270°. The *phenylthiosemicarbazide*,

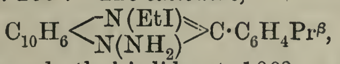
$$C_{20}H_{17}N_2\cdot NH\cdot CS\cdot NHPh,$$

crystallises in prisms or quadratic plates, m. p. 70°. The *benzylidene* derivative, $C_{20}H_{17}N_2\cdot N{:}CHPh$, forms yellow prisms, m. p. 151°; the *hydrochloride*, $C_{20}H_{17}N_2\cdot N{:}CHPh,HCl$, yellow needles, m. p. 244° (decomp.); the *sulphate*, $(C_{27}H_{23}N_3)_2,H_2SO_4$, yellow needles, sintering at 150°; the *nitrate*, $C_{27}H_{23}N_3,HNO_3$, yellow needles, m. p. 160° (decomp.); the *picrate*, $C_{33}H_{26}O_7N_6$, yellow needles, m. p. 228°; the *platinichloride*, $(C_{27}H_{23}N_3)_2,H_2PtCl_6$, forms a yellowish-red precipitate, decomp. 243°.

The products obtained on treating phenylbenzylbenzylidenehydrazine with hydrochloric and picric acids in hot alcoholic solution yield the unchanged hydrazine on recrystallisation from alcohol.

The *ethiodide*, $C_{10}H_6<\begin{matrix}\overline{\qquad\quad}N(EtI)\\N(N{:}CHPh)\end{matrix}>C\cdot C_6H_4Pr^{\beta}$, prepared by heating the benzylidene base with ethyl iodide at 100°, forms reddish-yellow crystals, m. p. 179° (decomp.). The o-*hydroxybenzylidene* derivative, $C_{20}H_{17}N_2\cdot N{:}CH\cdot C_6H_4\cdot OH$, crystallises in yellow needles, m. p. 223°.

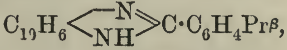
The p-iso*propylbenzylidene* derivative, $C_{20}H_{17}N_2\cdot N\colon CH\cdot C_6H_4Pr^\beta$, yellow needles, m. p. 260°. The *ethiodide*,



$$C_{10}H_6\left<\begin{matrix}N(EtI)\\N(NH_2)\end{matrix}\right>C\cdot C_6H_4Pr^\beta,$$

from the amino-base and ethyl iodide at 100°, crystallises in yellow prisms, m. p. 199°.

1-Amino-2-*p*-*iso*propylphenyl-2 : 3-naphthaglyoxaline remains unchanged when boiled with acetone or with *iso*valeraldehyde, or mercuric oxide, or sodium nitrite and hydrochloric acid in alcoholic solution.

The *hydrochloride* of 2-*p*-*iso*propylphenyl-2 : 3-naphthaglyoxaline, $C_{20}H_{19}N_2Cl$, is obtained by boiling the 1-amino-compound with hydrochloric acid and amyl nitrite in alcoholic solution, or, together with dibenzylamine, by reduction of the 1-benzylideneamino-compound with zinc dust and glacial acetic acid and treatment of the reaction liquid with hydrochloric acid. It crystallises in yellowish-white needles, m. p. about 288° (decomp.). The free *base*,  $C_{10}H_6\left<\begin{matrix}N\\NH\end{matrix}\right>C\cdot C_6H_4Pr^\beta$, forms white crystals, m. p. 247°. The *nitrate*, $C_{20}H_{18}N_2,HNO_3$, needles, m. p. 189° (decomp.), *sulphate*, white crystals, not melted at 295°, *picrate*, yellow needles, m. p. 267°, and *platinichloride*,

$$(C_{20}H_{18}N_2)_2,H_2PtCl_6,$$

yellowish-red precipitate, not melted at 292°, are described. G. Y.

Colour Bases of Triphenylmethane Dyes. Emilio Noelting and K. Philipp (*Ber.*, 1908, **41**, 579—585).—The existence of colourless carbinol and of coloured quinonoid forms of the colour bases of mono-, di-, and tri-aminotriphenylmethane dyes has been proved, mainly by Baeyer and Villiger (Abstr., 1904, i, 786). Whilst the constitution of the carbinol bases is beyond doubt, that of the quinonoid forms is established less certainly. Bases which contain unsubstituted or monosubstituted amino-groups appear to lose a molecule of water, yielding imino-bases of the types $CPh_2\colon C_6H_4\colon NH$, $CPh_2\colon C_6H_4\colon NPh$, &c. Triphenylmethane bases containing only disubstituted amino-groups have hitherto been known only in the colourless carbinol forms, although Hantzsch and Osswald (Abstr., 1900, i, 256) have shown the possibility of the existence of the coloured isomeric quinoneimonium bases without actually isolating them.

The authors have now succeeded in isolating hexamethyltriaminodiphenylnaphthylcarbinol (Naphtho-Blue), not only as the colourless carbinol, but also in the isomeric coloured quinonoid form; the question is not discussed whether the latter is an imonium or a carbonium hydroxide (compare Gomberg, Abstr., 1907, i, 504), the imonium formula $\colon C\colon C_6H_4\colon NMe_2\cdot OH$ being used.

The authors have also isolated in the pure state the colourless and the coloured forms of tetramethylethyltriaminodiphenylnaphthylcarbinol (Victoria Blue R, New Victoria Blue), and have shown definitely that the latter is obtained from the former by the loss of a molecule of water.

Hexamethyltriaminodiphenylnaphthylcarbinol (Naphtho-Blue) is prepared by heating a mixture of Michler's ketone, *a*-naphthyldimethylamine, and phosphoryl chloride, either alone or, more advantageously, in benzene solution, for ten hours on the water-bath; the base is obtained finally as a reddish-violet, amorphous powder. By repeated crystallisation from absolute ether, it is obtained in colourless crystals, m. p. 153°, whereas from boiling xylene it separates in dark green crystals, m. p. 260—261°; both forms have the composition $C_{29}H_{33}ON_3$. Cold dilute acids are instantly coloured blue in contact with an ethereal or benzene solution of the green crystals, but only after being warmed when a solution of the colourless crystals is used. Naphtho-Blue is reduced to a *leuco-base*, $C_{29}H_{33}N_3$, m. p. 172°, and forms salts which are extremely soluble in water. The dye has the constitutional formula $C(C_6H_4\cdot NMe_2)_2\colon C_{10}H_6\colon NMe_2Cl$, since it decomposes smoothly into Michler's ketone and α-naphthyldimethylamine by three days' heating with dilute sulphuric acid.

The *imino-base* of Victoria Blue R (New Victoria Blue),

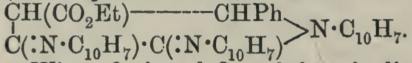
$$C(C_6H_4\cdot NMe_2)_2\colon C_{10}H_6\colon NEt,$$

m. p. 192·5°, is obtained as a reddish-brown precipitate when a hot dilute acetic acid solution of the dye is added to an excess of potassium hydroxide, or by slowly decomposing a hot alcoholic solution with the same alkali; the ethereal solution of the imino-base is intensely orange-yellow. The *carbinol base*, $OH\cdot C(C_6H_4\cdot NMe_2)_2\cdot C_{10}H_6\cdot NHEt$, is obtained by adding a hot solution of the dye to excess of ammonium hydroxide and heating over a naked flame until the originally coloured precipitate becomes grey. It turns red at 150° and has m. p. 159—162° or 167—170°, according to the rate of heating. The carbinol is converted into the imino-base when its solution in glycerol is heated to incipient ebullition. The *methyl ether*, m. p. 178°, crystallises in colourless needles; the *ethyl ether* has m. p. 153°.

C. S.

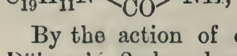
Action of Ethyl Oxalacetate on Benzylidene-β-naphthylamine. Syntheses in the Naphthaquinoline Group. LOUIS J. SIMON and CHARLES MAUGUIN (*Ann. Chim. Phys.*, 1908, [viii], 13, 361—395).—Mainly a résumé of work previously published (compare Abstr., 1904, i, 521, 812; Abstr., 1906, i, 887, 888; 1907, i, 725, 963).

In the condensation of ethyl oxalacetate with benzylidene-β-naphthylamine, besides the compound $C_{25}H_{25}O_5N$, there is produced a small quantity of a *substance*, $C_{43}H_{33}O_2N_3$, small needles, m. p. 94° (on Maquenne block), to which the authors assign the constitution



$$\left.\begin{array}{l}CH(CO_2Et)\text{------}CHPh \\ | \\ C(\colon N\cdot C_{10}H_7)\cdot C(\colon N\cdot C_{10}H_7)\end{array}\right> N\cdot C_{10}H_7.$$

When 2-phenyl-β-naphthaquinoline-3:4-dicarboxylic anhydride in ethereal solution is treated with ammonia, the corresponding *imide*,



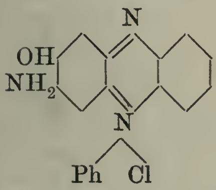
$C_{19}H_{11}N{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}NH$, m. p. 282°, is formed.

By the action of oxalacetic acid on benzylidene-β-naphthylamine, Döbner's 2-phenylnaphthaquinoline-4-carboxylic acid (Abstr., 1889, 411, 412), but not the di-acid, is formed.

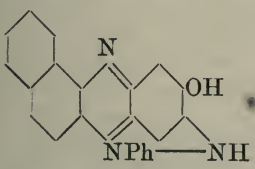
E. H.

Prasindones. FRIEDRICH KEHRMANN and R. SCHWARZENBACH (*Ber.*, 1908, **41**, 472—481).—With the object of investigating prasindones of a simpler nature than those studied hitherto (Kehrmann and Aebi, Abstr., 1899, i, 526), attempts have been made to prepare some simple prasindones by way of the condensation products of 4-amino-5-hydroxy-*o*-benzoquinone (Kehrmann and Prager, Abstr., 1907, i, 447) with 2-aminodiphenylamine and 2-anilino-1-aminonaphthalene. The compounds obtained, however, were stable prasindone hydrates, the inner anhydrides of which, that is, the prasindones themselves, could not be prepared. It is therefore evident that the formation of the prasindone-like anhydride is intimately connected with some definite constitution.

4-Amino-5-hydroxy-*o*-benzoquinone condenses with 2-aminodiphenylamine in the presence of hydrochloric acid, yielding small quantities of 2-amino*apo*safranone (Fischer and Hepp, Abstr., 1905, i, 948), the principal product formed being 3-*amino*-2-*hydroxyphenylphenazonium chloride*, annexed formula, obtained as dark brownish-red crystals. The free *base*, $C_{18}H_{13}ON_3$, obtained from the chloride on treatment with potassium hydrogen carbonate, crystallises in glistening, reddish-brown leaflets or needles, decomposing above 300°; the *diacetyl* derivative, $C_{22}H_{17}O_3N_3$, crystallises in dark green needles with a violet reflex, decomposing at about 290° The action of sodium nitrite on a solution of the base in sulphuric acid leads to the elimination of the amino-group, and, on subsequent treatment with sodium nitrate, 2-*hydroxyphenylphenazonium nitrate* is obtained as a reddish-brown, crystalline powder; the corresponding *platinichloride*, $(C_{18}H_{13}ON_2)_2PtCl_6$, forms small, glistening, dark brownish-red crystals. The free base could not be isolated; the blue solution obtained by treating the nitrate with sodium carbonate undoubtedly contains the prasindone hydrate.



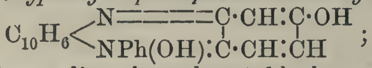
2-Anilino-1-aminonaphthalene condenses with 4-amino-5-hydroxy-*o*-benzoquinone in the presence of hydrochloric acid, yielding the *hydrochloride* of an *aminonaphthaprasindone*, $C_{22}H_{16}ON_3Cl$, isomeric with *s*-amino*iso*rosindone (Fischer and Arntz, Abstr., 1907, i, 94); it crystallises in bronzy leaflets, sometimes in green leaflets with a metallic lustre, and dissolves in alcohol, forming a yellowish- to blood-red solution with a brick-red fluorescence. The free *base*, having the annexed formula, crystallises in dark brown needles with a metallic lustre, and decomposes above 320°. The violet solution of the base in strong sulphuric acid on dilution with ice becomes blue, and finally brownish-red, from which solution the *sulphate* separates as a reddish-brown, crystalline powder. The *acetyl* derivative, $C_{24}H_{17}O_2N_3$, crystallises in bluish-black needles, m. p. 342°. The base, dissolved in sulphuric acid, is converted on treatment with sodium nitrite and sodium chloride into 2-*hydroxyphenylnaphthaphenazonium chloride*, obtained as a reddish-brown, crystalline powder; the corresponding *nitrate*, $C_{22}H_{15}O_4N_3$, crystal-



lises in small, yellowish-red needles; the *platinichloride*,

$$(C_{22}H_{15}ON_2)_2PtCl_6,$$

is obtained as a brick-red, crystalline powder. The chloride, on treatment with sodium carbonate, yields the *base*, which from analysis is probably 2-*hydroxyphenylnaphthaphenazonium hydroxide*,

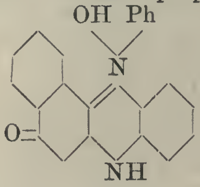


$$C_{10}H_6<\begin{matrix}N{=\!=\!=\!=}C\cdot CH{:}C\cdot OH\\ NPh(OH){:}C\cdot CH{:}CH\end{matrix};$$

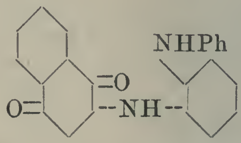
it crystallises in long, glistening, almost black needles, does not lose water at 180—200°, decomposes above 300°, and forms orange-coloured *salts* with both strong and weak acids. The salts with strong acids are not hydrolysed in aqueous solution. The *platinichloride* of the *acetyl* derivative, $(C_{24}H_{17}O_2N_2)_2PtCl_6$, is obtained as a brick-red, crystalline powder.

The reddish-brown isomeride derived from the bluish-green prasindone hydrate, to which the formula I was assigned previously (Kehrmann, Abstr., 1896, i, 508), is better represented by formula II, since it shows no basic properties:

I.



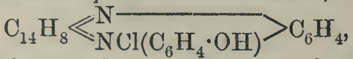
II.



W. H. G.

o-Amino-p-hydroxydiphenylamine. FRITZ ULLMANN and MATSUO FUKUI (*Ber.*, 1908, **41**, 624—626).—A mixture of *o*-phenylenediamine and phenol behaves in much the same manner as a mixture of *p*-phenylenediamine and phenol (D.R.-P. 15915) when oxidised with manganese dioxide. A compound of an indophenol character is deposited in the form of crystals with a coppery lustre, and, when these are reduced with sodium sulphide, 2-*amino*-4'-*hydroxydiphenylamine*, $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot OH$, is formed. It crystallises from dilute alcohol in large, colourless, flat needles, m. p. 149·5°. Its solution in hydrochloric acid is readily oxidised by ferric chloride, and its solution in sodium hydroxide by atmospheric oxygen.

Hydroxyphenylphenanthraphenazonium chloride,



$$C_{14}H_8\lessdot\begin{matrix}N\text{——————}\\ NCl(C_6H_4\cdot OH)\end{matrix}>C_6H_4,$$

obtained by condensing acetic acid solutions of the aminohydroxydiphenylamine and phenanthraquinone with a little hydrochloric acid, crystallises from dilute acetic acid in dark brown, glistening needles. The *nitrate*, $C_{26}H_{17}O_4N_3$, is less soluble, and forms small, red crystals.

4'-*Hydroxy*-2-*phenylaziminobenzene*, $C_{12}H_9ON_3$, obtained by the action of nitrous acid on the aminohydroxydiphenylamine, forms colourless crystals, m. p. 170°. J. J. S.

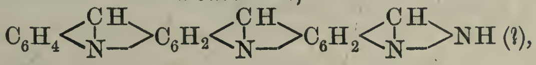
Formation of Indazole Derivatives from ortho-Methylated Anilines. PAUL JACOBSON and L. HUBER (*Ber.*, 1908, **41**, 660—671).—When boiled in acid solution, diazotised *o*-toluidines, containing substituting nitro-groups or bromine atoms in the benzene nucleus, undergo ring condensation, forming indazoles (Noelting, Abstr., 1904, i, 690). In the absence of negative substituting groups, the indazole formation takes place to only a very small extent whether in acid, neutral (Noelting, *loc. cit.*), or alkaline (Bamberger, Abstr., 1899, i, 543) solution. The present authors have now found that indazoles are obtained from *o*-toluidines in good yields, which do not contain negative substituting groups, by converting the base into the *N*-nitroso-acyl-*o*-toluidine, $C_6H_4Me\cdot N(NO)\cdot COR$, and gently heating this in benzene, when the indazole, $C_6H_4{<}\substack{CH_2\\ N}{\geqslant}N$ or $C_6H_4{<}\substack{CH\\ |\\ N}{>}N$, and the acid, $R\cdot CO_2H$, are formed. The indazoles are obtained in yields equal to 20—25% of the acylnitrosoamines.

Benzoyl-o-*tolylnitrosoamine*, $C_6H_4Me\cdot NBz\cdot NO$, prepared by the action of nitrous acid on benzo-*o*-toluidide suspended in glacial acetic acid, forms a yellow, crystalline mass, m. p. 62—63° (decomp.), detonates when heated on platinum, decomposes gradually at the ordinary temperature, yields a sublimate of yellow needles, and couples with α-naphthol in alkaline, or with α-naphthylamine in acetic acid, solution. When heated with alcohol, or more slowly at the ordinary temperature, it yields benzo-*o*-toluidide, but in anhydrous chloroform or benzene solution it develops heat and forms benzoic acid and indazole. This forms a stable, white, amorphous *silver*, $C_7H_5N_2Ag$, and a crystalline *mercuric*, $(C_7H_5N_2)_2Hg$, derivative.

Acetyl-v-m-*xylylnitrosoamine*, $C_6H_3Me_2\cdot NAc\cdot NO$, crystallises in yellow plates, m. p. 62—63°, and couples slowly with alcoholic α-naphthol, forming a red *dye*, but not with α-naphthylamine. When boiled with benzene, it forms acetic acid and 7-*methylindazole*, $C_8H_8N_2$, which separates from light petroleum in crystals, m. p. 138°, or from water in long, colourless needles, yields a white sublimate, has an odour resembling iodoform, volatilises in a current of steam, and forms a yellow, crystalline *nitroso*-derivative.

5-Methylindazole was obtained in the same manner from *as*-*m*-xylidine.

Since phenylenediazosulphide, $C_6H_4{<}\substack{S\\ N}{\geqslant}N$, on prolonged heating yields diphenylene disulphide, $C_6H_4{<}\substack{S\\ S}{>}C_6H_4$, if indazole has the constitution $C_6H_4{<}\substack{CH_2\\ N}{\geqslant}N$, it might be expected when heated to yield nitrogen and 9 : 10-dihydroanthracene, $C_6H_4{<}\substack{CH_2\\ CH_2}{>}C_6H_4$. It is found, however, that, when heated with copper powder at 270—290°, indazole yields ammonia and a *substance*,



$$C_6H_4{<}\substack{CH\\ |\\ N}{>}C_6H_2{<}\substack{CH\\ |\\ N}{>}C_6H_2{<}\substack{CH\\ |\\ N}{>}NH\ (?),$$

which crystallises from aniline in yellow prisms, m. p. 318—319° (corr.), is soluble in concentrated hydrochloric or sulphuric acid, and is not attacked by acetic anhydride or methyl iodide or sulphate, but on treatment with nitric acid, D 1·48, yields a *trinitro*-derivative,

$C_{21}H_9N_4(NO_2)_3$,

crystallising in scarlet prisms, commencing to sinter at 320°.

When heated with copper powder at 280°, 7-methylindazole yields a yellow condensation *product*, which could not be purified, whilst 5-methylindazole gave only resins.

Indazole remains unchanged when boiled, or heated under pressure at 200°, with glacial acetic acid and zinc oxide (compare Plancher, Abstr., 1902, i, 640; Plancher and Caravaggi, Abstr., 1905, i, 298; Plancher and Ciusa, Abstr., 1907, i, 80). G. Y.

Influence of Hydroxyl Ions on Azo-coupling. GUSTAV HELLER (*J. pr. Chem.*, 1908, [ii], 77, 189—192).—It was found previously (Abstr., 1907, i, 800) that the action of diazobenzene chloride on anthranil in sodium carbonate solution leads to the formation of trisbenzeneazophenol. The further investigation of the reaction has shown that in the absence of anthranil only bisbenzeneazophenol and small amounts of benzeneazophenol are formed, and that trisazo-compounds are not formed by the action of diazotised *p*- or *o*-toluidine on anthranil. On the other hand, trisbenzeneazophenol is formed by the action of diazobenzene chloride on phenol in presence of a free alkali, or by the action of diazobenzene chloride on methylanthroxan or other bases, such as quinoline, but not on pyridine or diethylamine. Hence it is concluded that the trisazo-compound is formed from diazobenzene chloride in consequence of the conversion of a part of this into phenol, and the coupling of the phenol with unchanged diazo-chloride under the influence of hydroxyl ions. The reaction is found, moreover, to depend on the concentration of the hydroxyl ions; when this increases above a certain limit, the formation of the trisazo-compound ceases and there ensues another reaction, which is still to be investigated. G. Y.

Replacement of the Sulphonic by the Cyano- and Carboxyl Groups in Azo-compounds. MARTIN LANGE (D.R.-P. 189935 and 191838).—The azo-derivatives of β-naphthol-3:6-disulphonic acid when heated with an aqueous solution of cyanide exchange the sulphonic group in position 3 for a cyano-group.

Sodium m-*xylene-4′-azo-3-cyano-β-naphthol-6-sulphonate*,

$C_6H_3Me_2{\cdot}N_2{\cdot}C_{10}H_5(OH)(CN){\cdot}SO_3Na$ or

$C_6H_3Me_2{\cdot}N_2H{:}C_{10}H_5O(CN){\cdot}SO_3Na$,

separates in sparingly soluble, glistening crystals on heating sodium *m*-xylene-4-azo-β-naphthol-3:6-disulphonate with aqueous sodium cyanide at 60—90°.

Sodium p-*nitrobenzeneazo-3-cyano-β-naphthol-6-sulphonate*,

$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(OH)(CN){\cdot}SO_3Na$ or

$NO_2{\cdot}C_6H_4{\cdot}N_2H{:}C_{10}H_5O(CN){\cdot}SO_3Na$,

prepared in a similar manner from sodium *p*-nitrobenzeneazo-β-naphthol-3:6-disulphonate, separates in well-defined needles with a metallic lustre. These new azo-derivatives dye wool in darker shades then the original azo-disulphonates.

The foregoing cyanoazo-derivatives when boiled with aqueous sodium hydroxide undergo hydrolysis and become converted into the corresponding carboxyl compounds. The production of the carboxyl derivatives can be effected in one operation by boiling the azo-derivatives of β-naphthol-3 : 6-disulphonic acid with aqueous sodium cyanide and hydroxide.

Sodium m-*xylene*-4′-*azo*-3-*carboxy*-β-*naphthol*-6-*sulphonate*,

$$C_6H_3Me_2{\cdot}N_2{\cdot}C_{10}H_5(OH)(CO_2H){\cdot}SO_3Na,$$

and six other azo-derivatives of sodium 3-carboxy-β-naphthol-6-sulphonate are described in the patent. G. T. M.

Electrolytic Preparation of Hydrazo-compounds. Friedrich Darmstädter (D.R.-P. 189312).—The conditions necessary for the electrolytic reduction of nitrobenzene to hydrazobenzene are efficient agitation, considerable excess of current, and suitable concentration of alkali hydroxide or salt. Nitrobenzene (100 grams) is suspended in 1 litre of 3% sodium hydroxide contained in the cathode cell; the anode liquid is 5% to 10% aqueous sodium hydroxide. The electrodes are preferably of iron or nickel, and 150% to 200% of the calculated current is sent through the cell with a current density of two to three amperes per square dcm. of cathode. The cathode solution is thoroughly agitated. In this way, the nitrobenzene is almost entirely reduced to hydrazobenzene, and the latter is separated from a small proportion of azoxybenzene by the action of hydrochloric acid, which transforms the hydrazo-derivative into soluble benzidine hydrochloride.

The reduction of *o*-nitrotoluene or *o*-nitroanisole when effected in the foregoing manner leads to the production of tolidine or dianisidine.

G. T. M.

Protein Nomenclature. (Report of a Joint Committee of the Amer. Physiol. Soc. and the Amer. Soc. of Biol. Chemists. Signed by R. H. Chittenden, O. Folin, W. J. Gies, W. Koch, T. B. Osborne, P. A. Levene, J. A. Mandel, A. P. Mathews, and L. B. Mendel. *Proc. Amer. physiol. Soc.*, 1907—8, xxvii.—xxx.; *Amer. J. Physiol.*, 21).—The term Protein as a class name is accepted. The following are the main points of difference between this report and that of the English Committee which considered the subject (see *Proc.*, 1907, 23, 55).

The term albuminoid is retained for the collagen keratin group. The class of phospho-proteins (caseinogen, vitellin) is transferred to the subdivision of conjugated proteins. The following five additional groups are inserted at various places: (1) Glutelins, vegetable proteins soluble in dilute alkali. (2) The alcohol-soluble proteins of vegetable origin. (3) Coagulated proteins, the result of the action of heat or alcohol. (4) Lecitho-proteins. (5) Proteans, insoluble products which result from the incipient action of water, very dilute acids, or enzymes.

W. D. H

Union of the Serum Proteins with Alkali. Lawrence J. Henderson (*Amer. J. Physiol.*, 1908, 21, 169—172).—Some experiments are recorded on the assumption that the serum proteins behave with alkalis like simple substances. They indicate the magnitude of the union in very faintly alkaline solutions. The matter is treated in a preliminary manner, the object of the work being to elucidate carbon dioxide transport in the blood; Zuntz believes that the passing off of this gas involves a transfer of sodium from carbon dioxide to protein. W. D. H.

Leucine Fraction from Protein Hydrolysis. Felix Ehrlich and Adolf Wendel (*Biochem. Zeitsch.*, 1908, **8**, 399—437).—Determinations of the optical rotation in hydrochloric acid of leucine, obtained by the hydrolysis of proteins, have yielded numbers varying between $[\alpha]_D + 16{\cdot}9°$ and $[\alpha]_D + 18{\cdot}9°$, whereas Fischer's synthetic active leucine has $[\alpha]_D + 15{\cdot}6°$. This is due to the fact that the leucine from protein hydrolysis has not yet been obtained pure. It has been shown already that the leucine fraction contains an *iso*leucine, from which it can be separated by taking advantage of the fact that the copper salt of *iso*leucine is soluble in methyl alcohol, whereas that of leucine is insoluble. By the simple extraction with methyl alcohol, the separation is not, however, complete, an insoluble residue is left containing large quantities of leucine and small quantities of *iso*leucine. On decomposing this residue with hydrogen sulphide, reconverting into the copper salts, and re-extracting with methyl alcohol, a further separation is effected, and by repetition of this process a pure leucine can be obtained finally from several proteins with a rotatory power agreeing with that of the synthetic substance.

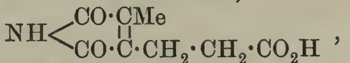
In all cases of protein hydrolysis, the methyl-alcoholic extract contained, besides *iso*leucine, valine. The separation of these two substances presents very great difficulties, owing to the similar solubilities both of the free acids and their copper salts. By treating the acids with baryta water under pressure, the valine was completely racemised, whereas the *d*-*iso*leucine was about half converted into *d*-*allo*-*iso*leucine, that is, a stereoisomeric substance which is not the optical antipode of the original body. The *d*-*l*-valine yielded a copper salt which was much less soluble than that of the optically active substance both in methyl and ethyl alcohols. By extracting the copper salts of the racemised acids with alcohols, the valine can be nearly completely separated from the leucines. On subjecting to yeast fermentation, the free acids, obtained by the employment of this method of separation, nearly pure *l*-valine, and *d*-*allo*-leucine can be obtained both from casein and yeast. The *l*-valine obtained from yeast gave $[\alpha]_D^{20} - 27{\cdot}62°$ (in hydrochloric acid); *l*-valine prepared by E. Fischer gave $[\alpha]_D^{20} - 28{\cdot}40°$. The *d*-*allo*-*iso*leucine from the same source gave $[\alpha]_D^{20} - 35{\cdot}7°$, also in 20% hydrochloric acid. S. B. S.

Elementary Composition of Different Caseinogens. Franz Tangl and J. Csókás (*Pflüger's Archiv*, 1908, **121**, 534—549).—Analyses of the caseinogen prepared by Hammarsten's method from the milk of the cow, buffalo, sheep, goat, horse, and ass are given; they show slight differences, which are considered to prove that caseinogen is a different substance in different milks, and to confirm what has been found by the precipitin reaction. The closer the biological relationships between the different animals on the list the closer is the correspondence in ultimate analysis of the caseinogens.

W. D. H.

Hæmatin; Salts, Esters, and Aniline Derivatives of the Hæmatic Acids, and Condensation Products of the Esters. William Küster (with F. Lacour and A. Nicole) (*Zeitsch. physiol. Chem.*, 1908, 54, 501—547. Compare Abstr., 1905, i, 622; 1906, i, 337).—The main object of the investigation was to obtain condensation products of the esters of hæmatic acid which might show a certain resemblance to hæmatin itself.

From the imide of tribasic hæmatic acid,



$$\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot CMe}\\ \| \\ \mathrm{CO\cdot C\cdot CH_2\cdot CH_2\cdot CO_2H}\end{matrix},$$

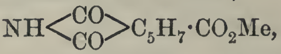
a *potassium* salt, $C_8H_8O_4NK$, needles, decomposing at 212°, a basic *lead* salt, and a *silver* salt, $C_8H_7O_4NAg_2$, have been prepared.

The esterification of the monobasic hæmatic acid, $C_8H_8O_5$, with dilute alcoholic hydrochloric acid produces a mixture of esters; the chief constituent (70%) of this mixture, soluble in sodium carbonate, is *methyl dihydrogen haematate*, $\mathrm{CO_2H\cdot CMe\colon C(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2Me}$, b. p. 173—176°/11 mm., from which a crystalline *calcium* salt, $C_9H_{10}O_6Ca$, an amorphous *silver* salt, $C_9H_{10}O_6Ag_2$, and an amorphous *ammonium* salt, $C_9H_{18}O_6N_2$, were obtained. Besides the acid methyl ester, there are formed simultaneously smaller quantities of *methyl anhydrohaematate*, $\mathrm{O}<\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}>\mathrm{C_5H_7\cdot CO_2Me}$, and normal trimethyl hæmatate. The last two substances are separated by passing dry ammonia gas into the ethereal solution, when the anhydride ester combines with two molecules of ammonia, and is precipitated as the amorphous *substance*, $C_9H_{16}O_5N_2$, which is regarded as the *ammonium* salt of *monomethylhaematate amide*, and which is converted by acidification of its aqueous solution into the acid methyl ester already described. *Trimethyl haematate*, $C_{11}H_{16}O_6$, b. p. 300—301°/760 mm. and 165—167°/10 mm., is formed in small quantity (12%) by the esterification with alcohol and hydrochloric acid, and is not precipitated by ammonia from its ethereal solution; it is formed quantitatively from silver hæmatate and methyl iodide.

The corresponding ethyl esters were prepared in a similar manner, although not so readily. *Ethyl dihydrogen haematate*, $C_{10}H_{14}O_6$, b. p. 165°/10 mm., was freed from unchanged acid by fractional distillation; its composition corresponded with that of an anhydride, $C_{20}H_{26}O_{11}$, but molecular weight determinations indicate that it is an equimoleculer mixture (of constant boiling point) of the ester $C_{10}H_{14}O_6$ and the anhydride ester, $C_{10}H_{12}O_5$. The *salts*, $C_{10}H_{12}O_6Ca$, $C_{10}H_{12}O_6Pb$, and $C_{10}H_{12}O_6Ag_2$, were analysed. By combination with ammonia, a *substance*, $C_{20}H_{38}O_{11}N_4$, is formed. As in the case of the corresponding methyl derivative, the *ethyl* ester of anhydrohæmatic acid, $C_{10}H_{12}O_5$, could only be isolated as the ammonia additive product,

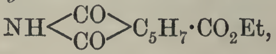
$C_{10}H_{18}O_5N_2$, which passes by the evaporation of its aqueous solution into *diammonium ethyl haematate*, $CO_2Et{\cdot}C_5H_7(CO_2NH_4)_2$. The triethyl ester of hæmatic acid (unlike the trimethyl ester) cannot be prepared by hydrochloric acid; there is formed instead *hydrogen diethyl haematate*, $CO_2H{\cdot}C_5H_7(CO_2Et)_2$, b. p. 179—180°/15 mm. *Triethyl haematate*, $C_{14}H_{22}O_6$, b. p. 191°/19 mm., is, however, obtainable from the silver salt and ethyl bromide.

The *methyl* ester of hæmatic acid imide,



$$NH{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_5H_7{\cdot}CO_2Me,$$

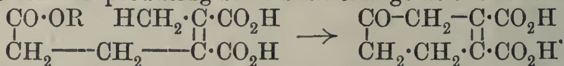
b. p. 170—172°/10 mm., separates from water in needles, m. p. 64°, and is prepared by treating the silver salt, $C_8H_7O_4NAg_2$, with methyl iodide and distilling the product under diminished pressure, or, more conveniently, by heating the ammonia additive product of methyl dihydrogen hæmatate, $C_9H_{12}O_6$, or of the anhydride ester, $C_9H_{10}O_5$; one molecule of ammonia is then eliminated (the corresponding additive product of the free acids loses both molecules of ammonia when heated). The *ethyl* ester of hæmatic acid imide,



$$NH{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_5H_7{\cdot}CO_2Et,$$

b. p. 195°/10 mm., is a viscid oil, and can be prepared according to both the methods employed for the methyl ester.

The intramolecular condensation of the esters was next attempted with the view of producing some such change as the following:



By heating the ester $C_{20}H_{26}O_{11}$ (or $C_{10}H_{14}O_6$) with sodium ethoxide, a small quantity of a *substance*, $C_{18}H_{20}O_{10}$, m. p. 146—147°, was obtained, which yielded with dry ammonia a *substance*, $C_{18}H_{26}O_{10}N_2$. No further elimination of alcohol could be achieved. By using a larger proportion of sodium ethoxide, a substance, b. p. 175—178°/14 mm., was obtained, to which the formula $C_{48}H_{40}O_{26}$ is assigned; this is regarded as being formed by the elimination of three molecules of alcohol and one of water from three molecules of the ester $C_{20}H_{26}O_{11}$; no molecular weight determination is given. By the action of sodium methoxide on the methyl ester, $C_9H_{12}O_6$, a minute quantity of a *substance*, m. p. 189°, was obtained, which probably represents the desired cyclic condensation product, $C_8H_8O_5$, represented above.

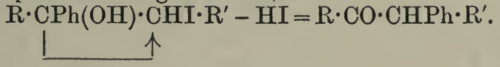
By addition of aniline to the ethereal solution of the acid, $C_8H_8O_5$, the *aniline* salt of *haematic anilide*, $C_{20}H_{22}O_5N_2$, m. p. 86—87°, is obtained, which, on boiling with water, is transformed into a *substance*, $C_{14}H_{15}O_5N$, m. p. 110°, probably *haematic anilide*, and more readily to *anilhaematic acid*, $C_{14}H_{13}O_4N$, m. p. 120°.

The *ammonium* salt of *monomethylhaematic anilide*, $C_{15}H_{20}O_5N_2$, m. p. 132—133°, and *methyl anilhaematate*, $C_{15}H_{15}O_4N$, m. p. 47—48°, were prepared in a similar manner from monomethylhæmatate.

G. B.

Organic Chemistry.

Structural Changes in Organic Chemistry. Marc Tiffeneau (*Chem. Zentr.*, 1908, i, 112—113; from *Rev. gén. Sci. pur. appl.*, 1907, 18, 583—594).—A theoretical paper dealing with the changes in the "carbon skeleton" through the wandering of a carbon radicle. Such structural transformations are divided into two groups, as taking place in a stable or in an unstable molecule. In the first group are placed those changes which involve the formation of a more stable molecule; for instance, the change of a carbylamine into a primary amine. The second group is considered to be due to the setting free of valencies caused by the interaction of one or more elements in the molecule; the freed valencies only being satisfied through a molecular rearrangement. This last group is subdivided into two classes: (*a*) carbon wandering, owing to the setting free of two valencies on the same element; an example being the change of diphenylchloroethylene into tolane and the Beckmann intramolecular change. (*b*) Carbon wandering, due to the setting free of two valencies on two neighbouring or distant elements; for instance, the pinacolin transformation and the Auwers transformation. The author points out that the wandering of an aryl radicle only takes place when the compound contains an OH group attached to the same carbon atom as the wandering group, which is not split off during the change:



$$R\cdot CPh(OH)\cdot CHI\cdot R' - HI = R\cdot CO\cdot CHPh\cdot R'.$$

J. V. E.

Applications of Grignard's Reaction. Alexander McKenzie (*Brit. Assoc. Report*, 1907, 77, 273—298).—A detailed account of the reactions to which Grignard's reagent is applicable, and of the theoretical considerations underlying these reactions. T. H. P.

Boiling Point of *iso*Butane. William A. Noyes (*J. Amer. Chem. Soc.*, 1908, 30, 142—143).—*iso*Butane, prepared by the reduction of *iso*butyl iodide with zinc and dilute alcohol, has b. p. −11·5°/760 mm. The hydrocarbon (b. p. 0°) obtained by Mabery from American petroleum (Abstr., 1897, i, 389) and regarded by him as *iso*butane was not this substance, but probably *n*-butane. E. G.

Relative Volatility of Certain Groups of Mixed Carbon Compounds. Louis Henry (*Bull. Acad. roy. Belg.*, 1907, 842—855. Compare Abstr., 1907, i, 1102).—The boiling points of series of disubstituted ethane compounds represented by the general formulæ $CH_2R\cdot CH_2R$, $CH_2R\cdot CH_2R'$ and $CH_2R'\cdot CH_2R'$ are compared.

In certain cases the boiling point of the mixed compound is the arithmetic mean of the boiling points of the corresponding simple compounds. This is the case when R and R′ represent chlorine and bromine, fatty acid radicles of similar structure, isomeric fatty acid radicles, methoxy- and ethoxy-groups, or bromine and the ethoxy-group.

The boiling point of the mixed compound is higher than the mean of the boiling points of the simple compounds when R and R′ represent the hydroxyl and amino-group, or chlorine and the acetyl group.

Finally, the boiling point of the mixed compound is lower than the mean of the boiling points of the simple compounds when R and R′ represent bromine and hydroxyl, hydroxyl and ethoxyl, or ethoxyl and the amino-group.

The differences between the three groups of comparable compounds are attributed to the circumstance that certain substituting groups do not appreciably alter the degree of association in the liquid state, whilst other groups exert a marked effect, the extent of the influence varying considerably from one substituting group to another.

H. M. D.

Chloroform and Acetone. David B. Dott (*J. Soc. Chem. Ind.*, 1908, 27, 6, 271).—The formation of chloroform from ethyl alcohol is shown to be best indicated by $3C_2H_6O + 8Ca(OCl)_2 = 2CHCl_3 + 3CaCO_3 + CO_2 + 8H_2O + 5CaCl_2$, and the equation generally given for the formation of chloroform from acetone, $2CO(CH_3)_2 + 3CaOCl_2 = 2CHCl_3 + (CH_3{\cdot}CO_2)_2Ca + 2Ca(OH)_2$, agrees well with results found. The observation of Finnemore and Wade (Trans., 1904, 85, 938), that a small proportion of ethyl chloride is formed in preparing chloroform from ethyl alcohol, is confirmed. When purifying acetone, it is advisable to avoid treatment with mineral acids or other methods likely to cause formation of condensation products, such as mesityl oxide, phorone, or mesitylene, which, although shown by about 7% distilling above 58°, do not affect the iodoform or other methods of estimation. A rise of temperature, 11·7°, is observed when two molecular proportions of chloroform are mixed with one molecular proportion of acetone, and the resulting mixture distils for the most part above the b. p. of either constituent.

J. V. E.

Oxidation of Ethyl, Propyl, *iso*Butyl, and Amyl Alcohol by a Contact Process. E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 203—215. Compare this vol., i, 77).—A stream of dry air is saturated with the vapour of the given alcohol, and then passed through a heated tube containing freshly-reduced copper gauze. As in the case of methyl alcohol, $c^2.c_1/v^2$ is a constant, and for ethyl alcohol $= 0·0003—0·00024$; for *iso*butyl alcohol $= 0·0004—0·00045$; for amyl alcohol $= 0·0005—0·00048$; for propyl alcohol $= 0·00107$. The products of oxidation are carbon mon- and di-oxides, both saturated and unsaturated hydrocarbons, aldehydes (chiefly), and very small quantities of acids and ketones. In the case of propyl alcohol, when the conditions are such that the copper is heated without the application of external energy, an almost exactly theoretical quantity of air is needed for the oxidation, but with ethyl, *iso*butyl, and amyl alcohols an excess of air must be employed. When, however, in all these cases the concentration of the alcohol is near the theoretical, there is no spontaneous rise in the temperature of the copper; this being due to the fact that side by side with the exothermic reaction of oxidation there is also an endothermic reaction of decomposition (very slight in the case of propyl alcohol) of the alcohol into water and unsaturated hydrocarbons, and, in order to maintain the exothermic character of the reaction, it is necessary to have an excess of air, which oxidises the carbon monoxide with development of heat. Detailed tables of the products obtained for each of the alcohols are given.

Z. K.

Action of Organo-magnesium Haloids on Ethylideneacetone. A. Gry (*Bull. Soc. chim.*, 1908, [iv], 3, 377—381).—This work was undertaken with the view of synthesising and investigating tertiary alcohols containing an ethylenic linking. The results have been in part anticipated by those of Kohler (Abstr., 1907, i, 1050), but the latter author by using excess of the Grignard reagent obtained as the principal products the corresponding saturated ketones, whereas when the quantities of ethylideneacetone and organomagnesium haloid used are equimolecular the principal product is the corresponding tertiary olefinic alcohol. These alcohols undergo dehydration when treated with the ordinary acetylating reagents, and the hydrocarbons described below were obtained in this way. These are colourless, resemble light petroleum in odour, and give precipitates with aqueous solutions of mercuric chloride.

Dimethyl*iso*allylcarbinol, $CHMe{:}CH\cdot CMe_2\cdot OH$, b. p. 79—80°/145 mm., D^0 0·8154, D^{20}_4 0·8347, n^{20}_D 1·4302, obtained by the action of magnesium methyl iodide on ethylideneacetone, is a colourless, mobile liquid (compare Pawlowsky, Abstr., 1872, 1093), and on dehydration yields a hydrocarbon which may be identical with Ipatieff's trimethylallene, $CHMe{:}C{:}CMe_2$. *δ-Methyl-Δ^{β}-hexene-δ-ol* (*methylethyl*iso*allylcarbinol*), $CHMe{:}CH\cdot CMeEt\cdot OH$, b. p. 72—73°/60 mm., D^0 0·8471, $D^{12\cdot5}_4$ 0·8360, $n^{12\cdot5}_D$ 1·4268, is a colourless liquid with a pleasant, fruity odour. On dehydration, it yields a *diethylenic hydrocarbon*, b. p. 107—109°, which may have the formula $CHMe{:}C{:}CMe\cdot C_2H_5$. *δζ-Dimethyl-$\Delta^{\beta}$-heptene-δ-ol* (*methyl*iso*butyl*iso *allylcarbinol*), $CHMe{:}CH\cdot CMe(OH)\cdot CH_2\cdot CHMe_2$, b. p. 68—69°/17 mm., D^0 0·8105, D^{15}_4 0·8281, n_D 1·4285, similarly obtained, is a pleasant-smelling liquid. *δη-Dimethyl-Δ^{β}-octene-δ-ol* (*methyl*iso*amyl*iso*allylcarbinol*), $CHMe{:}CH\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CHMe_2$, b. p. 87—88°/18 mm. (decomp.), D^0 0·8442, $D^{14\cdot5}_4$ 0·8330, n_D 1·4368, is a liquid of insipidly sweet odour.

T. A. H.

Action of Alkalis on Alkylene Glycol-chlorohydrin Ethers. Josef Houben (*Ber.*, 1908, 41, 1027—1029. Compare Houben and Führer, this vol., i, 73).—Polemical. A reply to the criticisms of Hoering (this vol., i, 119).

W. H. G.

Density, Refractive Index, Surface Tension, and Viscosity of Various Mixtures of Glycerol and Water at 18°. Pablo Martínez-Strong (*Anal. Fis. Quim.*, 1908, 6, 75—77).—The following table shows the results of the measurements :

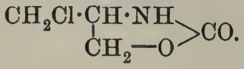
				Viscosity.	
Composition.	Relative density.	Refractive index.	Surface tension, number of drops.	No. of seconds.	μ.
Water	1·0000	1·3277	102	105	1·0000
10 per cent. glycerol	1·0295	1·3390	106	134	1·3137
20 ,, ,,	1·0681	1·3528	110	170	1·7197
30 ,, ,,	1·0860	1·3650	114	245	2·534
40 ,, ,,	1·1094	1·3787	119	345	3·6451
50 ,, ,,	1·1340	1·3891	124	476	5·4108
60 ,, ,,	1·1602	1·4020	130	640	7·0716
70 ,, ,,	1·1860	1·4129	136	1258	14·2094
80 ,, ,,	1·2142	1·4386	147	4165	48·1632
90 ,, ,,	1·2330	1·4529	158	6900	81·0256
Glycerol	1·2599	1·4650	172	64800	777·5382

The surface tension was determined by means of a Duclaux pipette, which, when filled with water at 15°, delivered 100 drops. The viscosity was measured by an Ostwald viscosimeter. μ is the coefficient of viscosity. W. A. D.

Derivatives of Epichlorohydrin. EMANUALE PATERNÒ and MASANIELLO CINGOLANI (*Gazzetta*, 1908, **38**, i, 243—247; *Atti R. Accad. Lincei*, 1908, [v], **17**, i, 237—241).—The authors have investigated the properties and derivatives of epichlorohydrin cyanate (compare Thomsen, Abstr., 1879, 217), which can be obtained by the action of either cyanic acid or potassium cyanate on epichlorohydrin. When potassium cyanate is employed, it is probable that an additive compound is formed, which is hydrolysed immediately, yielding potassium hydroxide; the latter then acts on some of the epichlorohydrin, giving potassium chloride and glycerol, so that half of the epichlorohydrin is destroyed. The maximum yield of epichlorohydrin cyanate obtained is about 37% of the theoretical amount.

With fuming nitric acid, epichlorohydrin cyanate yields a *nitro*-derivative, $C_4H_5O_4N_2Cl$, which crystallises from water in shining needles, m. p. 70°, and is a nitroamine, as it gives a hydrazine on reduction. The hydrazine could not be isolated, but it gives a *benzylidene* derivative, $CON{\cdot}C_3H_5ClO{\cdot}N{:}CHPh$, which crystallises from alcohol in yellow plates, m. p. 191°. Epichlorohydrin cyanate yields an oily *nitroso*-derivative, whilst it gives *iso*propylamine when reduced with sodium in alcoholic solution.

From these results, it is concluded that epichlorohydrin cyanate possesses the structure



$$\begin{array}{l}\mathrm{CH_2Cl{\cdot}CH{\cdot}NH}\\ \qquad\quad\mathrm{CH_2{-}O}\end{array}\!\!>\mathrm{CO}.$$

T. H. P.

Organic Polysulphides. BROR HOLMBERG (*Annalen*, 1908, **359**, 81—99).—Whilst the organic hydrosulphides, sulphides, and disulphides have been investigated repeatedly, little is known as to the methods of formation or the properties of the organic polysulphides. The author, therefore, has made these the object of a systematic study, and now describes the results obtained, including a method for the preparation of organic trisulphides hitherto formed only with great difficulty.

Whilst alkali sulphides unite with sulphur, forming polysulphides, alkali mercaptides are oxidised by sulphur or alkali polysulphides in aqueous solution at the ordinary temperature. Thus potassium ethylmercaptide, when shaken with sulphur in aqueous solution, yields ethyl disulphide and only small amounts of polysulphides, a result obtained also by treating the mercaptide with potassium disulphide. Potassium phenyl sulphide, on the other hand, although oxidised in the same manner by sulphur, forming phenyl disulphide, is not attacked by potassium di- or tri-sulphide, and is oxidised only slowly by potassium tetrasulphide.

Previous authors (Müller, *J. pr. Chem.*, 1871, [ii], **4**, 40; Klason, *ibid.*, 1877, [ii], **15**, 216; Böttger, Abstr., 1884, 1282) have found that ethyl sulphide, disulphide, and tetrasulphide form higher polysulphides when heated with sulphur at 150—180°. It is now shown that ethyl disulphide unites with sulphur in absolute alcoholic solution if saturated with anhydrous ammonia at the ordinary temperature. Ethyl dithioglycollate under the same conditions forms a brownish-red solution, from which the unchanged ester and sulphur are recovered on evaporation. When shaken with aqueous potassium hydroxide, potassium sulphide, and sulphur, ethyl bromide forms an oil consisting chiefly of ethyl disulphide together with ethyl sulphide and polysulphides (Spring and Demarteau, Abstr., 1889, 1110). It is concluded that such reactions, the mechanism of which is discussed, do not throw any light on the constitution of the polysulphides.

Mercaptans react with sulphur dichloride, prepared by passing chlorine into an ethereal solution of disulphur dichloride, forming mixtures of several products, chiefly di- and tetra-sulphides. This is in agreement with Aten's observation (Abstr., 1906, ii, 157) that sulphur dichloride is partly dissociated even at low temperatures.

The action of thionyl chloride on mercaptans in cooled ethereal solution takes place almost quantitatively according to the equation: $4R{\cdot}SH + SOCl_2 = R_2S_2 + R_2S_3 + H_2O + 2HCl$. The di- and tri-sulphides are separated by fractional distillation. Ethyl trisulphide, S_3Et_2, is a yellow, strongly refracting oil, b. p. 84—85°/15 mm., and has the characteristic odour of the organic sulphides.

A short résumé is given of other methods of forming polysulphides described by previous authors.

Trithiodiacetic acid, $S_3(CH_2{\cdot}CO_2H)_2$, formed together with the disulphide from thioacetic acid, crystallises from water in white leaflets, m. p. 123·5—124°, and has the electrical conductivity $K = 0{\cdot}104$; the *lead* and *silver* salts are described.

The *tetrasulphide* of acetic acid, $S_4(CH_2{\cdot}CO_2H)_2$, prepared by the action of disulphur dichloride on thiolacetic acid in ethereal solution, crystallises in prismatic needles, m. p. 112·5—113°, is partly decomposed with separation of sulphur on titration with alkalis, and yields the disulphide when boiled with water. The *silver* and *lead* salts are described. Reduction of the tetrasulphide with zinc and sulphuric acid leads to the formation of hydrogen sulphide and thiolacetic acid; on oxidation with bromine in aqueous solution, the tetrasulphide yields sulphuric and sulphoacetic acids. The *ethyl* ester is obtained as an oil. G. Y.

Action of Magnesium on Ethyl Bromoacetate. Robert Stollé (*Ber.*, 1908, **41**, 954—955).—The reaction between ethyl bromoacetate and magnesium in ethereal solution leads to the formation of ethyl acetoacetate and of ethyl γ-bromoacetoacetate (compare Zeltner, this vol., i, 243). C. S.

Vapour Density of Propionic Acid. A. Faucon (*Compt. rend.*, 1908, **146**, 691—694. Compare this vol., ii, 257).—Like the lower homologues of the fatty acids, propionic acid has an abnormal vapour density at its boiling point, the values obtained, using Dumas' method, being 3·75 and 3·80 at 148°, 3·58 and 3·60 at 152°, 3·39 at 160°, 2·98 at 162°, 2·96 at 170°, 2·77 at 180°, 2·70 at 190°, and 2·57 at 210°, the theoretical value calculated from $D = M/28\cdot95$ being 2·55. The vapour density of the acid at its boiling point (140°), obtained by extrapolation, is 4·0; it follows, therefore, that the molecular complexity at that temperature is 4/2·55 or 1·56.

Knowing the value of the vapour density of propionic acid at its boiling point, the author has calculated its heat of vaporisation by two methods, using Clapeyron's formula $L = T/425.(u' - u).dp/dT$ and Raoult's formula $L = 1\cdot988.T_2/(M.d'/d.f).df/dT$; the values obtained are 90·9 Cal. and 91·2 Cal. respectively, and these are in close agreement with the experimental value 90·43 Cal. (*loc. cit.*).

The factor $(u' - u)$ in Clapeyron's formula represents the difference between the volumes occupied by one gram of the saturated vapour and one gram of the liquid acid; in order to calculate the value of u, the specific gravity and coefficient of expansion of the liquid acid at 130° were determined, and found to be 0·8567 and 0·00153 respectively. M. A. W.

***l*- and *d*-Hexoic Acids.** Carl Neuberg and B. Rewald (*Biochem. Zeitsch.*, 1908, **9**, 405—413).—Neuberg and Rosenberg have shown that the hexoic acids, obtained from the putrefaction products of egg-white, contain about 50% of an optically active acid, which is, by reason of its origin, presumably β-methylvaleric acid. The racemic form of the acid has been synthesised by van Romburgh. This substance was prepared by a modification of van Romburgh's method, and separated into its antipodes by means of the brucine salt. The *l*-form was obtained pure, and gave $[\alpha]_D^{17}$ $-8\cdot98°$. S. B. S.

Preparation of the Alkyl Esters of the Higher Iodated Fatty Acids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 188434).—*Ethyl iodobehenate*, thin prisms, m. p. 290°, obtained by boiling together iodobehenic acid, alcohol, and concentrated sulphuric acid, crystallises from light petroleum.

Ethyl iodostearate, prepared in a similar manner, is a pale yellow oil of faintly fruity odour. G. T. M.

Preparation of Diacyl Glycerides of the Higher Fatty Acids. Ferdinand Ulzer, J. Batik, and Rudolf Sommer (D.R.-P. 189839).—The diglycerides of the higher fatty acids (C_{16}—C_{22}) are readily prepared by heating a mixture of the acid with excess of glycerol at 170° under 10 mm. pressure. After four to six hours, the diglyceride is separated from the glycerol by extraction with light petroleum. G. T. M.

Catalytic Reactions of Oxidation and Reduction of Unsaturated Organic Compounds. Sergius Fokin (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276—321. Compare Abstr., 1907, i, 820).—The oxidation of such substances as linseed oil is probably a process of molecular autoxidation accompanied by the decomposition of the products of the reaction into more volatile compounds, as well as by more complex reactions.

The absorption of oxygen by unsaturated compounds can be accomplished without any formation of decomposition products if metallic oxides are employed as catalysts, the explanation of their action being similar to that given previously, but the formation of unstable intermediate oxygen compounds must also be assumed.

The results obtained in the absorption of oxygen by thin layers of drying oil and by passing oxygen into solutions of various unsaturated oils are similar in character.

The reaction takes place in two stages, for which the equations $x=k_1.t$ and $k_2=1/t\log a/a-x$ are proposed; Ostwald's formulæ for autocatalysis do not yield satisfactory results, but Nernst's theory connecting the influence of diffusion and the chemical action itself should be taken into account here; thus, in accordance with this theory, the first (linear) stage is prolonged as the quantity of catalyst is diminished; again, the results of Geate's experiments with ultraviolet light agree far better with the equation $dx/dt=1/t\log a/(a-x)$ than with $dx/dt=(k_1+k_2x)(a-x)$, which shows that no autocatalyst can be present.

Experiments with linseed oil, cod liver oil, almond oil, some fatty acids, and mulberry oil are described; in the case of the latter it is possible that autocatalysis does occur.

Moisture retards the absorption of oxygen by drying oils, but to a less extent than is usually assumed. Light considerably hastens the process, even in the presence of strong catalysts. Rise of temperature hastens the process. The absorption tends to become proportional to the pressure of the oxygen; for pressures of 15—20 atmos., at the same time, the colour changes, but on removal of the high pressure the substance regains the original colour.

A simple and convenient apparatus is described for carrying out reduction experiments. The process of reduction is a unimolecular reaction and is not autocatalytic, the shape of the reduction curve depending on the diffusion of the gaseous particles, the condition of the surface of the catalyst, and the possibility of the decreasing effect of the latter owing to fatigue or poisoning. Unsaturated compounds containing a closed-chain do not react under the conditions of the experiments, although this inertness can probably be overcome under certain conditions of temperature even without the application of high pressures. Unsaturated compounds with low b. p. change but slightly. The stereo-isomeric forms of a substance react identically. The number of electro-negative groups, the occurrence of double linkings in close proximity to these groups, and the size of the molecule all influence the rate and limits of the catalytic reduction of the substance. The catalytic properties of solid molecular platinum are almost identical with those of colloidal solutions of platinum.

The rate of the reaction with 2% platinum is already sufficiently great to furnish a method for detecting various impurities by the estimation of the quantity of hydrogen absorbed. Palladium acts as a far weaker catalyst than platinum. Z. K.

The Carrying Down of Soluble Oxalates by Oxalates of the Rare Earths. Gregory P. Baxter and Herbert Wilkens Daudt (*J. Amer. Chem. Soc.*, 1908, 30, 563—572).—An investigation on the effect of conditions on the quantity of alkali oxalates carried down by the oxalates of neodymium, lanthanum, samarium, and yttrium. In general, it is found that: (1) the oxalates of the rare earths show a marked, but varying, tendency to carry down the oxalates of alkalis and ammonium, which increases with an increase in temperature and in the concentration of the molecular alkali oxalate at the moment of precipitation; (2) potassium and ammonium oxalates are occluded to a much greater extent than sodium oxalate. Precipitation with the latter gives, in most cases, precipitates only slightly contaminated with this salt; (3) by conducting the precipitation in the presence of a quantity of a strong acid, considerably more than equivalent to the alkali oxalate, the occlusion is in many cases wholly prevented; in the case of yttrium, the diminution is, however, slight; (4) in order to obtain a precipitate of a rare earth oxalate as pure as possible by means of an alkali or ammonium oxalate, precipitation should be conducted in cold dilute solution in the presence of a quantity of strong acid, considerably more than equivalent to the oxalate added.

The following table gives the molecular ratio of occluded oxalate to rare earth oxalate when precipitated from neutral and acid solutions:

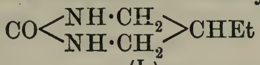
	$Na_2C_2O_4$.		$K_2C_2O_4$.		$(NH_4)_2C_2O_4$.	
	Acid.	Neutral.	Acid.	Neutral.	Acid.	Neutral.
$Nd_2(C_2O_4)_3$	0·02	0·02	0·01	0·79	0·01	0·71
$La_2(C_2O_4)_3$	0·04	0·02	0·00	0·09	0·01	0·27
$Sm_2(C_2O_4)_3$	0·00	0·30	0·00	0·94	0·00	0·32
$Y_2(C_2O_4)_3$	0·04	0·04	0·69	0·73	0·65	0·82

W. H. G.

New Drugs. IV. [Derivatives of Malonic Acid.] Alfred Einhorn [and, in part, Heinrich von Diesbach, Richard Feibelmann, and Carl Ladisch] (*Annalen*, 1908, 359, 145—187. Compare Abstr., 1901, i, 439, 493; 1903, i, 257).—A study of the influence of substituting groups on the reactions of derivatives of malonic acid.

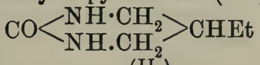
Various authors have observed that diethylmalonic acid and its derivatives undergo abnormal reactions. Thus, whilst the action of ammonia on methyl dimethylmalonate and methylethylmalonate leads to the formation of the corresponding amides, methyl diethylmalonate does not form an amide under the same conditions (Fischer and Dilthey, Abstr., 1902, i, 269; Meyer, Abstr., 1906, i, 137). Tafel and

Thompson (this vol., i, 58) found that, on electrolytic reduction, barbituric acid yields hydrouracil and trimethylenecarbamide, whilst 5-ethylbarbituric acid is reduced similarly to 5-ethylhydrouracil (I) and 4-ethyltrimethylenecarbamide (II), but that 5 : 5-diethylbarbituric acid forms 4 : 6-diketo-5 : 5-diethylhexahydropyrimidine (III):



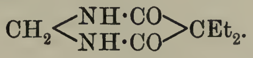
$$\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CH_2}\\ \mathrm{NH{\cdot}CH_2}\end{matrix}>\mathrm{CHEt}$$

(I.)



$$\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CH_2}\\ \mathrm{NH.CH_2}\end{matrix}>\mathrm{CHEt}$$

(II.)



$$\mathrm{CH_2}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}>\mathrm{CEt_2}.$$

(III.)

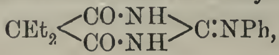
Again, the action of phosphoryl chloride and carbamide on diethylmalonic acid leads to the formation of diethylacetylcarbamide (Fischer and Dilthey, Abstr., 1905, i, 35), whereas barbituric acid and 5 : 5-dimethylbarbituric acid are formed by the action of these reagents on malonic and dimethylmalonic acids respectively. It is evident, therefore, that the abnormal reactions result from the presence of the two ethyl groups.

In agreement with Fischer and Dilthey's view (*loc. cit.*), that the first stage in the action of phosphoryl chloride and carbamide on diethylmalonic acid leads to the formation of diethylmalonuric acid, $NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CEt_2{\cdot}CO_2H$, it is now found that this acid is formed by the action of carbamide on diethylmalonyl chloride in cold pyridine solution and subsequent addition of dilute hydrochloric acid, but that, if the reaction mixture is heated on the water-bath and the pyridine removed by distillation in a current of steam before the acidification, the product obtained is 5 : 5-diethylbarbituric acid. It is assumed that in these reactions an intermediate *additive* compound of diethylmalonuryl chloride and pyridine, $NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CEt_2{\cdot}CO{\cdot}NC_5H_5Cl$, is formed.

The action of carbonyl chloride on diethylmalonic acid and carbamide in pyridine solution, on the other hand, leads to the formation of diethylacetylcarbamide (compare Einhorn and Hollandt, Abstr., 1898, i, 577). The first stage of this reaction probably leads to the formation of the monochloride, $CO_2H{\cdot}CEt_2{\cdot}COCl$, which must decompose at low temperatures, forming hydrogen chloride and the anhydride of diethylmalonic acid, since it is found that the action of aqueous pyridine on diethylmalonyl chloride leads to the formation of this anhydride (Abstr., 1906, i, 398).

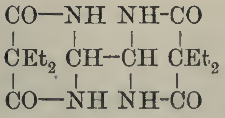
As it has been generally considered that anhydrides of the malonic acid series are incapable of existence, it was of special interest to study the action of aqueous pyridine on other malonyl chlorides. It is found that such anhydrides are obtained only from disubstituted malonyl chlorides, and that the stability increases with the size of the substituting groups. Thus dimethylmalonyl chloride yields a duodeci-molecular anhydride, which is more easily hydrolysed than the diethyl-anhydride, but ethylmalonyl and malonyl chlorides yield substances which are probably mixtures, cannot be purified, and do not yield pure decomposition products.

The influence of the two ethyl groups on the reactions of malonic acid derivatives has been studied also in the action of sodium amalgam on the thiobarbituric acids. Whereas thiobarbituric and 5-ethylbarbituric acids react with sodium amalgam and water only with great difficulty, and yield oily decomposition products, 5 : 5-diethylthiobarbituric acid is rapidly converted in the cold into, chiefly, diethylmalonamide, formic acid, and hydrogen sulphide, 4 : 6-diketo-5 : 5-diethylhexahydropyrimidine (Tafel and Thompson, *loc. cit.*) and bisdiethylmalonyltetra-aminoethane (2-bisdeoxyveronyl), which has the annexed constitution, being formed as by-products. In explanation of these reactions, the transient formation of the bivalent group, $CEt_2<\begin{smallmatrix}CO\cdot NH\\CO\cdot NH\end{smallmatrix}>C\colon$, is assumed. In agreement with this, it is found that the sulphur atom of diethylthiobarbituric acid is readily displaced by the action of aniline and phenylhydrazine with formation of diethylmalonylphenylguanidine,



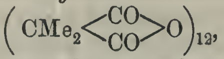
$$CEt_2<\begin{smallmatrix}CO\cdot NH\\CO\cdot NH\end{smallmatrix}>C\colon NPh,$$

and diethylmalonylphenylaminoguanidine, $CEt_2<\begin{smallmatrix}CO\cdot NH\\CO\cdot NH\end{smallmatrix}>C\colon N\cdot NHPh$, whilst the thio-acid is converted into diethylbarbituric acid when boiled with mineral or organic acids.



Molecular weight determinations with the higher polymeride of diethylmalonic acid (Abstr., 1906, i, 398) in benzene and in ethylene dibromide agree with the formula $(C_7H_{10}O_3)_{12}$, but in nitrobenzene with the formula $(C_7H_{10}O_3)_8$. This anhydride is hydrolysed slowly by aqueous potassium hydroxide at the ordinary temperature ; when heated with a limited amount of sodium ethoxide in alcoholic solution, it yields ethyl diethylacetate and diethylmalonate and *ethyl hydrogen diethylmalonate*, which is obtained as an oil, decomposes at 150°, forming carbon dioxide and diethylacetic acid, is soluble in alkalis, and on evaporation with aqueous sodium carbonate yields sodium diethylmalonate (compare Brown and Walker, Abstr., 1893, i, 394). Tables are given showing the amounts of diethylmalonamide, diethylmalonic acid, and diethylmalonamic acid formed by the action of ammonia, and of diethylacetyldiethylamide, diethylmalondiethylamic acid, and diethylmalonic acid formed by the action of diethylamine, on the anhydride under varying conditions as to solvent, molecular proportions, and temperature.

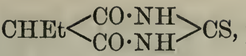
The duodeci-molecular *anhydride* of dimethylmalonic acid,



$$\left(CMe_2<\begin{smallmatrix}CO\\CO\end{smallmatrix}>O\right)_{12},$$

is obtained as a white, amorphous powder, m. p. 145—148° (decomp.), cannot be converted into a quadrimolecular modification, is readily hydrolysed by moisture, forming dimethylmalonic acid, and when heated with aqueous ammonia yields dimethylmalonamide and dimethylmalonic acid.

The action of aqueous pyridine on ethylmalonyl chloride leads to the formation of a yellow oil, which mostly contains ethylmalonic acid and chlorine, and sometimes pyridine. The product obtained similarly from malonyl chloride is a yellowish-brown powder, m. p. 190—195° (decomp.).

5-*Ethylthiobarbituric acid*,  $CHEt<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>CS$, prepared by heating ethyl sodioethylmalonate with thiocarbamide in alcoholic solution, crystallises in yellow needles, m. p. 192°.

5 : 5-*Dimethylthiobarbituric acid*, $C_6H_8O_2N_2S$, prepared from thiocarbamide and ethyl sodiodimethylmalonate, crystallises in yellow needles, m. p. 216°, and on treatment with sodium amalgam and water is converted partly into dimethylmalonamide.

Bisdiethylmalonyltetra-aminoethane, $C_{16}H_{26}O_4N_4,2H_2O$, crystallises in white prisms, loses $2H_2O$ at 110°, m. p. 340°, is soluble in aqueous sodium carbonate, being reprecipitated on acidification, and is stable towards oxidising agents.

4 : 6-Diketo-5 : 5-diethylhexahydropyrimidine, m. p. 293° (292°: Tafel and Thompson, *loc. cit.*), has feeble basic properties, is stable towards oxidising agents, and does not condense with benzaldehyde in presence of zinc chloride; the *mercurichloride*, $C_8H_{14}O_2N_2,HgCl_2$, long needles, m. p. 215—218°.

5 : 5-*Dipropylthiobarbituric acid*, $C_{10}H_{16}O_2N_2S$, prepared by heating dipropylmalonyl chloride with thiocarbamide or by condensation of ethyl dipropylmalonate with thiocarbamide in presence of sodium ethoxide, crystallises in yellow needles, m. p. 154°, and on treatment with sodium amalgam and water at the ordinary temperature yields dipropylmalonamide and a small amount of a *substance* which is probably bisdipropylmalonyltetra-aminoethane.

Diethylmalonylphenylguanidine (2-*phenyliminodiethylbarbituric acid*), $C_{14}H_{17}O_2N_3$, prepared by heating diethylthiobarbituric acid with aniline at 120—130°, crystallises from alcohol in white needles, m. p. 253°, and is readily soluble in dilute alkalis. *Diethylmalonylphenylaminoguanidine* (2-*phenylhydrazinodiethylbarbituric acid*), $C_{14}H_{18}O_2N_4$, formed from diethylthiobarbituric acid and phenylhydrazine at 120—130°, crystallises in yellow needles, m. p. 215°, and yields a blue *sodium* salt, which forms a red solution in much water. These two malonylguanidines are decomposed by boiling mineral acids, forming diethylbarbituric acid and the bases from which they are prepared.

When heated at 100—130° with *as*-dimethylcarbamide, diethylmalonyl chloride forms the *diethylmalonyl* derivative,

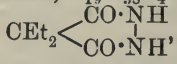
$$CEt_2(CO\cdot NH\cdot CO\cdot NMe_2)_2,$$

which separates from hot water in rhombic crystals, m. p. 158°, and is soluble in aqueous alkalis. The *diethylmalonyl* derivatives of *as*-diethylcarbamide, $C_{17}H_{32}O_4N_4$, white needles, m. p. 125°, and *as*-phenylmethylcarbamide, $C_{23}H_{28}O_4N_4$, white needles, m. p. 172°, are formed in the same manner. These diethylmalonylcarbamides are hydrolysed, forming diethylbarbituric acid, when heated with a mixture of concentrated and fuming sulphuric acids.

Diethyl- and dipropyl-barbituric acids are formed when the corresponding malonamides are heated with phenyl carbonate at 200—215°.

The *diethylmalonate* of glycollamide, $CEt_2(CO\cdot O\cdot CH_2\cdot CO\cdot NH_2)_2$, formed by heating sodium diethylmalonate and chloroacetamide with a a small amount of sodium iodide at 110—120°, separates from water in white crystals, m. p. 126°.

Diethylaminoethyl diethylmalonate, $CEt_2(CO\cdot O\cdot CH_2\cdot CH_2\cdot NEt_2)_2$, prepared by the action of diethylmalonyl chloride on cooled diethylaminoethyl alcohol, is obtained as a yellow oil which decomposes partly on distillation; the *citrate*, $C_{19}H_{38}O_4N_2,2C_6H_8O_7$, was analysed.

Diethylmalonylhydrazide,  $CEt_2<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot NH\end{matrix}$, prepared from hydrazine hydrate and diethylmalonyl chloride in aqueous solution, crystallises in prisms, m. p. 256°.

The *diethylmalonyl* derivative of anthranilamide,

$$CEt_2(CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH_2)_2,$$

prepared by the action of diethylmalonyl chloride on anthranilamide in cooled pyridine solution, crystallises in microscopic prisms, m. p. 215°. G. Y.

Refractometric Evidence for the Constitution of Carbon Suboxide. ARTHUR MICHAEL (*Ber.*, 1908, **41**, 925—928).—The conclusion drawn by Diels and Blumberg (this vol., ii, 103) from the determinations of the molecular refraction and dispersion, that the author's representation of it as β-hydroxypropiolic lactone (Abstr., 1906, ii, 442) is incorrect, is controverted. The calculated values given for this formula are not accepted, as Moureu (Abstr., 1906, ii, 1) has shown that Brühl's numbers for the acetylenic linking in hexylpropiolic acid are too low, 2·22 and 0·19 instead of 3·60 and 0·455, and therefore this optical method cannot decide between the two formulæ at present. W. R.

Action of Zinc or Magnesium on Mixtures of Esters of Oxalic and of α-Brominated Fatty Acids. New Syntheses of *as*-Dialkylmalic and Dialkyloxalacetic Esters. BERTHOLD RASSOW and R. BAUER (*Ber.*, 1908, **41**, 963—965).—The reaction between ethyl oxalate and ethyl bromo*iso*butyrate in the presence of zinc at 60—65° leads to the formation of ethyl *as*-dimethylmalonate, whilst the same two substances in ethereal solution react with magnesium to form ultimately ethyl dimethyloxalacetate, the *semicarbazone* of which, $C_{11}H_{19}O_5N_3$, has m. p. 96°.

Ethyl oxalate and ethyl bromodiethylacetate react in a similar manner under the latter conditions, yielding the *substance*, $C_{12}H_{20}O_5$, b. p. 135—136°/12 mm. C. S.

Behaviour of Cholic Acid towards Ozone. KURT LANGHELD (*Ber.*, 1908, **41**, 1023—1025. Compare this vol., ii, 211).—Cholic acid resembles cholesterol, to which it is generally assumed to be chemically related, in its stability towards oxidising agents, which if sufficiently powerful to attack the molecule break it down to simple acids. Hence, although cholic acid has formed the subject of many investigations, its constitution has been elucidated only so far that it is known to be a monocarboxylic acid containing two primary and one secondary carbinol groupings. With the object of throwing further light on the constitution of cholic acid, the author has now studied its behaviour towards ozone.

When treated with 10% ozone in presence of chloroform, cholic acid combines with 4 atoms of oxygen, forming a solid *ozonide*, $C_{24}H_{40}O_9$, which when boiled with water is partly decomposed, yielding hydrogen peroxide and a reducing *substance*. The ozonide decomposes at 120—130° in a vacuum, forming aldehydes which have an aromatic odour, can be distilled, and react with phenylhydrazine and semicarbazide. This behaviour of cholic acid towards ozone is analogous to that which has been observed with unsaturated acids and with hydroaromatic substances (Harries, Abstr., 1906, i, 225).

Cholesterol, when treated in the same manner with ozone, forms an *ozonide*, which contains two or more O_3-groups and decomposes on distillation in a vacuum. G. Y.

Formation of Acetaldehyde in Alcoholic Fermentation. J. Auguste Trillat (*Compt. rend.*, 1908, **146**, 645—647. Compare Abstr., 1903, ii, 231; 1907, ii, 492).—Contrary to the observations of Roeser (*Ann. Inst. Pasteur*, 1893, 41), the author finds that in alcoholic fermentation the production of aldehyde is only a concomitant phenomenon and does not occur in the absence of oxygen. Comparative experiments were made in which nutrient liquids containing lactose were sown with yeasts obtained from cheese, in the first case allowing free access of air, and in the second case expelling all the oxygen both from the nutrient liquid and the space above it by a current of hydrogen or carbon dioxide. The aldehyde was estimated colorimetrically by means of rosaniline hydrogen sulphite, the precaution being taken in the second series of experiments to distil off the alcohol in the absence of air. The results show that no aldehyde is produced in an atmosphere of hydrogen or carbon dioxide, that introduction of a small amount of air caused the production of 2—10 mg. of aldehyde per litre, and that 50 mg. per litre are produced with free access of air. E. H.

Formation of Acetaldehyde in Alcoholic Fermentation. E. Kayser and A. Demolon (*Compt. rend.*, 1908, **146**, 783—784).—Trillat's conclusion (preceding abstract) relative to the origin of acetaldehyde in alcoholic fermentation had already been arrived at by the authors (Abstr., 1907, ii, 714). Production of acetaldehyde is intimately connected with the presence of a living aerobic yeast on the surface. Addition of antiseptics capable of killing the yeast considerably reduces the proportion of aldehyde, and aseptic addition of yeast afterwards killed by heat has no action on the aldehyde production. The magnitude of the differences observed leads the authors to conclude that living yeast is an essential agent of the phenomenon. E. H.

Molecular Dispersion of Succindialdehyde. Carl D. Harries (*Ber.*, 1908, **41**, 909—910. Compare this vol., i, 133).—A correction. The dispersion was calculated for the F—C lines and not for the G′—C as Brühl's figures require. A redetermination of these constants shows the molecular dispersion to be 0·52, a result in close agreement with that calculated for the dialdehyde, namely, 0·55. W. R.

Formation of Aldehydes or Ketones during Acetic Fermentation. K. Farnsteiner (*Zeitsch. Nahr. Genussm.*, 1908, **15**, 321—326).—An investigation showed that all liquids which have undergone more or less complete acetic fermentation contain a neutral, volatile substance which reduces Fehling's solution (compare Abstr., 1901, i, 625). The substance is similar to acetol in its physical properties and in its behaviour to Fehling's solution and sulphurous acid; when treated with phenylhydrazine, however, it yields an osazone, m. p. 243°, and also an oily product. W. P. S.

Formation of Thio-aldehydes. Ludwig Vanino (*J. pr. Chem.*, 1908, [ii], **77**, 367—368. Compare Abstr., 1902, i, 744; Schmidt, *ibid.*, 1906, i, 711; 1907, i, 282).—Trithioformaldehyde is readily formed when sodium thiosulphate crystals are fused, mixed with an equal weight of 40% formaldehyde solution, and this mixture poured into half its weight of 38% hydrochloric acid. The crystalline thioaldehyde is deposited almost immediately, and is removed, washed with water, and recrystallised from benzene. Other aldehydes react in a similar manner. J. J. S.

Keten. Norman T. M. Wilsmore and Alfred W. Stewart (*Ber.*, 1908, **41**, 1025—1027. Compare Abstr., 1907, i, 478; Wilsmore, Trans., 1907, **91**, 1938).—Polemical. A claim for priority over Staudinger and Klever (this vol., i, 246). W. H. G.

Ketens. VII. Classification. Hermann Staudinger and H. W. Klever (*Ber.*, 1908, **41**, 906—909. Compare this vol., i, 246).—Dilute ethereal solutions of methyl- and ethyl-keten are obtained when zinc reacts with ethereal solutions of α-bromopropionyl bromide and α-bromobutyryl bromide and the products are distilled. The yields are poor and the solutions react with aniline, forming the anilides of propionic and butyric acids. Carbon suboxide (Diels, Abstr., 1906, ii, 227) is also a keten, and may be obtained by the action of zinc on *dibromomalonyl bromide*, which is an oil, b. p. 91—92°/13 mm. The ketens are divided into the following groups: 1. Keten, its monoalkyl derivatives, and carbon suboxide. They are colourless and not capable of autoxidation. They are polymerised by pyridine or quinoline, and do not form additive compounds with substances containing the C:N or C:O groups.

2. Dialkylated ketens. These are coloured, and readily undergo autoxidation. They yield keten bases with pyridine and quinoline, and form additive compounds with benzylideneaniline (C:N group) and quinone (C:O group).

Both groups readily combine with water, alcohols, or amines, and also with bromine or chlorine.

The first groups are termed *aldo-ketens* and the second, *keto-ketens*. J. J. S.

β-Hydroxy-αα-dialkyl Ketones. Migration under the Influence of Alkalis. Edmond E. Blaise and I. Herman (*Compt. rend.*, 1908, **146**, 700—702).—The unsaturated C_7 ketone, obtained as one of the products of the action of potassium hydroxide solution on ethyl hydroxy*tert.*-butyl ketone (this vol., i, 248), is iso*propyl methylvinyl ketone*, $CHMe_2\cdot CO\cdot CMe\colon CH_2$, for it is identical with the synthetical product obtained from ethyl α-bromopropionate by the method described by Blaise and Maire (Abstr., 1907, i, 749), and involving the following series of reactions:

$$CHMeBr\cdot CO_2Et + CH_2O + Zn \longrightarrow OH\cdot CH_2\cdot CHMe\cdot CO_2Et \longrightarrow$$
$$OAc\cdot CH_2\cdot CHMe\cdot CO_2H \longrightarrow OAc\cdot CH_2\cdot CHMe\cdot COCl + CHMe_2ZnI \longrightarrow$$
$$OAc\cdot CH_2\cdot CHMe\cdot CO\cdot CHMe_2 \longrightarrow CH_2\colon CMe\cdot CO\cdot CHMe_2.$$

*iso*Propylmethylvinyl ketone has b. p. 55—56°/60 mm., the *semicarbazone* has m. p. 90·5°, and the p-*nitrophenylhydrazone* has m. p. 89°, and its formation from ethyl hydroxy*tert.*-butyl ketone is probably the result of an intramolecular change, involving the migration of the carbinol group $-CH_2\cdot OH$ and subsequent dehydration of the hydroxy-ketone formed,

$$OH\cdot CH_2\cdot CMe_2\cdot CO\cdot CH_2Me \longrightarrow CHMe_2\cdot CO\cdot CHMe\cdot CH_2\cdot OH \longrightarrow$$
$$CHMe_2\cdot CO\cdot CMe\colon CH_2$$

(compare Blaise and Courtot, Abstr., 1905, i, 853).

The author discusses and rejects two other possible explanations of the course of the reaction.

In addition to *iso*propyl methylvinyl ketone, a hydroxy-ketone is obtained in small quantity by the action of potassium hydroxide solution on ethyl hydroxy-*tert.*-butyl ketone; it is an isomeride of the original ketone, has b. p. 62—63°/15 mm., yields a phenylurethane derivative and a *p*-nitrophenylhydrazone, and is converted into *iso*propyl methylvinyl ketone by the dehydrating action of 50% sulphuric acid; it probably has the constitution represented by the formula $CHMe_2\cdot CO\cdot CMe_2\cdot OH$. M. A. W.

Behaviour of Dextrose, Lævulose, and Galactose towards Dilute Sodium Hydroxide. JAKOB MEISENHEIMER (*Ber.*, 1908, 41, 1009—1019).—Buchner, Meisenheimer, and Schade (Abstr., 1907, i, 17) found that the action of hydrogen peroxide on lævulose in alkaline solution leads to the formation of formic and glycollic acids, and a hydroxy-acid having the composition of erythritic acid. The identity of the last is now doubtful, as the supposed *i*-erythritylphenylhydrazide obtained from it has since been found to be acetylphenylhydrazide (compare Lespieau, Abstr., 1907, i, 173; Nef, this vol., i, 5), and it may have been a mixture of polyhydroxy-acids having the composition of erythritic acid. The present author has now studied the behaviour of hexoses towards dilute sodium hydroxide in absence of an oxidising agent, as this also is of interest in connexion with the problem of alcoholic fermentation.

Dextrose and lævulose behave similarly, yielding, after some months in dilute sodium hydroxide at the ordinary temperature, 50—60% of *i*-lactic acid, 30—50% of a mixture of polyhydroxy-acids, 0·5—2% of formic acid, and a small amount of a brown, amorphous substance, whilst about 1% of the hexose forms carbon dioxide and alcohol. Under the same conditions, galactose yields less than 20% of lactic acid, but about 70% of the mixture of polyhydroxy-acids, together with traces of formic acid. The mixture of polyhydroxy-acids forms a calcium salt, which, on analysis, gives results corresponding with an acid, $(CH_2O)_{5\cdot5}$; hence the polyhydroxy-acids are not all saccharinic acids, $C_6H_{10}O_5$, as assumed by Nef (*loc. cit.*). On prolonged extraction with ether, the mixture of acids yields small amounts of dihydroxybutyric acid. The presence of sodium sulphite or of potassium cyanide does not prevent the coloration of sugar solutions by alkalis (compare Schade, Abstr., 1906, i, 931); the decomposition of the sugar is only slightly, if at all, retarded by the sulphite. G. Y.

A Crystallised Lævulose Tetra-acetate. D. H. Brauns (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, **10**, 563—566).—Lævulose reacts with an excess of acetyl bromide at −15°, and the yellow product, after removal of the acetyl bromide under low pressure, dissolution in alcohol, and evaporation in a desiccator, yields colourless crystals.

Laevulose penta-acetate has m. p. 131—132°, D^{15} 1·388, and has a bitter taste. In chloroform solution, it has $[\alpha]_D^{20}$ −91·38°. Crystals monoclinic; $a:b:c = 1\cdot3463:1:1\cdot5733$, $\beta = 52°12'$. C. H. D.

Condensation of Formaldehyde and Lactose. Paul Rosenberg (D.R.-P. 189036).—*Formaldehyde-lactose*, $C_{12}H_{22}O_{11},5CH_2O,H_2O$, is obtained by heating lactose with 40% formaldehyde solution at 65° in a vacuum, and finally evaporating the solution to dryness. The product is soluble in water, alcohol, or acetone. On warming its alcoholic solution at 60—70°, the compound decomposes, regenerating lactose. G. T. M.

Formulæ of Polysaccharides. Heinrich Kiliani (*Chem. Zeit.*, 1908, **32**, 366).—The formula for starch or cellulose should not be $(C_6H_{10}O_5)_n$, the correct general formula for a polysaccharide being $(C_6H_{10}O_5)_n,H_2O$ or $C_{6n}H_{10n+2}O_{5n+1}$. This is proved by the author's previously published analyses of the three anhydrous trisaccharides, raffinose, melezitose, and mannasaccharide, all of which pointed to the formula $C_{18}H_{32}O_{16}$. Similarly, the analysis of inulin led to the formula $C_{36}H_{62}O_{31}$. Although Brown and Morris (Trans., 1889, **55**, 463), from molecular weight determinations, are in favour of doubling the formula for inulin, it is at least doubtful whether the ordinary methods of determination yield trustworthy results in the case of substances of such high molecular weight. P. H.

Composition of Starch Grains. Z. Gatin-Gružewska (*Compt. rend.*, 1908, **146**, 540—542).—The separation of starch into amylopectin and amylose (Maquenne and Roux) can be effected by placing the grains in very dilute sodium carbonate until their envelope of amylopectin is burst; by subsequent neutralisation, the envelope contracts again and can be separated, the amylose remaining in solution. G. B.

Composition of Starch Grains. Léon Maquenne (*Compt. rend.*, 1908, **146**, 542—545).—Amylose (compare preceding abstract) gives a pure blue colour with iodine, and amylopectin a violet colour; these substances are probably related, and intermediate substances may exist. Starch paste which has not been superheated is not a true colloid, but contains amylose in a state of true solution together with particles of the grain envelope (amylopectin), which are to some extent organised and are much larger than ordinary colloid particles. Amylopectin can also be separated from amylose by boiling with salt solutions. G. B.

The Influence of the Alternating Current on the Rate of Hydrolysis of Starch by Diastase and Mineral Acids. A. Lebedeff (*Biochem. Zeitsch.*, 1908, 9, 392—402).—Alternating currents of weak strength (0·013—0·015 ampere) increase the rate of formation of sugar by diastase; stronger currents act in a similar way at first, but afterwards the enzyme loses its activity. Weak currents also increase the rate of starch hydrolysis by acids. Various hypotheses are suggested to account for these facts; the author is inclined to regard the change in the surface tension of the colloidal particles as the most likely cause. S. B. S.

Cellulose and its Derivatives. Carl G. Schwalbe (*Chem. Zeit.*, 1908, 32, 287—288).—Polemical. A reply to Grandmougin (this vol., i, 250). P. H.

Preparation of Formyl Esters of Cellulose. J. P. Bemberg (D.R.-P. 189836 and 189837).—Formic acid in the presence of sulphuric acid reacts with cellulose, yielding a formate. Cotton wool (15 parts) is added to 100 parts of 98% formic acid containing 3—10 parts of concentrated sulphuric acid. After several hours, a colourless, syrupy solution of *cellulose formate* is obtained, which is precipitated by water as a white mass. Instead of cellulose, hydrocellulose, cellulose hydrate, and mercerised cellulose may be employed. Formic acid alone does not condense in this way, but the sulphuric acid may be replaced by 2% to 4% of hydrogen chloride. G. T. M.

Acetylation. Douglas J. Law (*Chem. Zeit.*, 1908, 32, 365—366).—The author has investigated the action of the new acetylating agent recommended by Cross, Bevan, and Briggs, which is obtained by adding 100 grams of acetic anhydride to a solution of 50 grams of zinc chloride in 100 grams of glacial acetic acid. With cellulose, it gives a triacetate, but with starch it does not react at all; it converts sucrose into the octa-acetyl derivative and dextrose into a tetra-acetyl compound, indefinite crystals, m. p. 98°. Added in slight excess to benzaldehyde, a violent reaction takes place; after some time, the fluorescent solution is poured into cold water, when crystals of a *diacetate*, $C_6H_5\cdot CH(OAc)_2$, are obtained; this substance crystallises from alcohol, and has m. p. 43° and b. p. 225—230°. When furfuraldehyde dissolved in glacial acetic acid is treated with an excess of the reagent and the mixture is cooled in a freezing mixture, a dark solution is obtained. On pouring into water, after half an hour, an oil separates out which gradually crystallises; this substance, which is also a *diacetyl* derivative, $C_4OH_3\cdot CH(OAc)_2$, crystallises from alcohol, and has m. p. 45° and b. p. 220°. If the reagent is allowed to react with furfuraldehyde at the ordinary temperature, a black substance is obtained which is not attacked by acids or alkalis. P. H.

Constitution of ψ-Ammonium Bases. II. JOHANNES GADAMER (*Arch. Pharm.*, 1908, **246**, 89—90).—An introduction to the paper dealt with in the next abstract; this paper brings experimental evidence to support Gadamer's view as to the three tautomeric forms of ψ-ammonium bases (Abstr., 1905, i, 368). G. B.

Chloral Alcoholates. Connexion with the Constitution of ψ-Ammonium Bases. F. KUNTZE (*Arch. Pharm.*, 1908, **246**, 91—111. Compare preceding abstract).—The conversion of a chloral alcoholate into that of another alcohol by evaporation of its solution in an excess of this second alcohol is due to mass action and to the dissociation of the alcoholate, as supposed by Gadamer. This is proved by the polarimetric investigation of the equilibrium in chloroform solution between *l*-amyl alcohol, chloral *l*-amyl alcoholate, and an inactive alcohol with its chloral compound, at a temperature of 20°. The equilibrium was approached from both sides, for instance, by mixing equal molecular proportions of chloral *l*-amyl alcoholate, $[\alpha]_D^{20}$ $+1\cdot19°$, and ethyl alcohol and of chloral ethyl alcoholate and *l*-amyl alcohol. In the case of ethyl and of propyl alcohol, the equilibrium is reached when about 60% of chloral *l*-amyl alcoholate and 70% of *l*-amyl alcohol are present. With secondary alcohols, the proportion of *l*-amyl alcohol is smaller, and with tertiary alcohols it falls to less than 10%. Two molecular proportions of ethyl alcohol added to one of chloral *l*-amyl alcoholate raised the proportion of liberated *l*-amyl alcohol to 50% and 8 molecules to 84%. One molecule of *l*-amyl alcohol, added to chloral hydrate dissolved in chloroform, liberates water and forms 98% of *l*-amyl alcoholate. With cotarnine in benzene solution, similar results were obtained, indicating the existence of an (unstable) alcoholate.

Fourteen chloral alcoholates of the type $CCl_3\cdot CH(OH)\cdot OR$ were prepared; the following were obtained crystalline and were analysed: from methyl alcohol, m. p. 38°; from ethyl alcohol, m. p. 50°; from *iso*propyl alcohol, m. p. 45°; from *n*-butyl alcohol, m. p. 49°; from trimethylcarbinol, m. p. 43°, and from cinnamyl alcohol, m. p. 42°. G. B.

Preparation of Hexamethylenetetramine Borate. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 188815).—When one, two, and three molecular proportions of boric acid are mixed with hexamethylenetetramine (1 mol.), one, two, and three molecular proportions of water are eliminated respectively on drying at 70—80°. The residues consist of the three borates of hexamethylenetetramine: $HBO_2,C_6H_{12}N_4$, $2HBO_2,C_6H_{12}N_4$, and $3HBO_2,C_6H_{12}N_4$. These salts, which also separate from the alcoholic solutions of their generators, are neutral or feebly acid crystalline powders, soluble in water and having useful antiseptic properties. G. T. M.

Reduction of Amino-acids to Amino-aldehydes. CARL NEUBERG (*Ber.*, 1908, **41**, 956—963).—Fischer's method in the sugar series of reducing lactones to aldehydes led the author to attempt the reduction of amino-acids in a similar manner, with negative results. When however, the esters of α-amino-acids or their hydrochlorides are reduced by sodium amalgam in a well-cooled aqueous or alcoholic solution, which is kept always acid by the addition of hydrochloric acid when necessary, amino-aldehydes are obtained, the amount of which is determined by isolating the amino-aldehyde in the form of the phenylosazone or of the *p*-nitrophenylosazone (ammonia and hydrogen being eliminated), or by converting it into the pyrazine derivative by means of alkaline mercuric chloride. In this way, the reduction of the esters of glycine, alanine, aminobutyric acid, leucine, aspartic acid, anilinoacetic acid, tyrosine, diaminopropionic acid, serine, *iso*serine, cystine, glycylglycine, and hippuric acid has been detected.

The hydrochlorides of the esters of β-amino-acids also undergo reduction, but the resulting solutions, whilst reducing alkaline solutions of silver salts, are not affected by Fehling's solution; this affords, therefore, a method of differentiating between α- and β-amino-acids.

The *phenylosazone*, $C_{14}H_{14}N_4$, obtained from aminoacetaldehyde, forms yellow crystals and has m. p. 176—177°. The p-*nitrophenylosazone*, $C_{15}H_{14}O_4N_6$, m. p. 277° (decomp.), from α-aminopropaldehyde, is a scarlet, crystalline powder. C. S.

Physico-chemical Study of the Complex Copper–Glycine Sulphates. J. T. Barker (*Trans. Faraday Soc.*, 1908, 3, 188—204).—Measurements of the relative concentrations of cupric ions in solutions containing copper sulphate and glycine (by means of the *E.M.F.* of concentration cells) lead to the conclusion that complex ions are formed containing 4 molecules of glycine to each atom of copper. The freezing point of a glycine solution is raised by addition of copper sulphate, and the results are in harmony with the view that the complex anions above mentioned are partly dissociated in solutions which do not contain a very large excess of glycine. The electrical conductivity of a copper sulphate solution increases when glycine is added to it, until 10 molecules of glycine have been added for each molecule of copper sulphate; further additions result in a decrease of conductivity. It is suggested that this is due to disturbance of the hydrolytic dissociation equilibrium in the copper sulphate solution, the cupric hydroxide combining with the glycine and so giving rise to the production of more free sulphuric acid. Zinc sulphate behaves in the same way. Measurements of the *E.M.F.* of a hydrogen electrode in zinc sulphate–glycine solutions and of the rate of inversion of sucrose by copper sulphate–glycine solutions show that the concentration of hydrogen ions is actually increased by the addition of glycine. By crystallisation of copper sulphate–glycine solutions, products were obtained consisting of mixtures of copper glycine, $(NH_2\cdot CH_2\cdot CO_2)_2Cu$, and basic glycine sulphate,

$(NH_2\cdot CH_2\cdot CO_2H)_3H_2SO_4$. T. E.

Reduction of Glycine Ethyl Ester. Emil Fischer (*Ber.*, 1908, 41, 1019—1023).—Ethyl oxalate differs from other esters of aliphatic and aromatic acids in that it can be reduced by sodium amalgam (Traube, this vol., i, 75). This behaviour results evidently from the direct union of the two strongly negative carbethoxy-groups. A similar, although more feeble, effect was observed previously as resulting from the accumulation of hydroxyl groups in the dibasic acids of the sugar group (Fischer, Abstr., 1890, 597). As an amino-group in the α-position has an influence similar to that of hydroxyl on the carboxylic group, it was to be expected that the esters of α-amino-acids would be capable of being reduced by sodium amalgam. This is now found to be the case with glycine ethyl ester, which, when treated with sodium amalgam in neutral or slightly acid solution, yields a liquid which reduces Fehling's solution, and must contain aminoacetaldehyde or its semiacetal, $NH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}OEt$. The reducing power of the solution shows that the ester is reduced to the extent of about 25%. On addition of hydrochloric acid to the reaction solution, evaporation almost to dryness under 10—15 mm. pressure, and treatment of the residue with hydrogen chloride in alcoholic solution at 0°, most of the unchanged glycine ester separates as the hydrochloride, whilst the reduction product is converted into aminoacetal, which is stable towards alkalis, and hence is readily separated from the remainder of the ester. G. Y.

Walden's Inversion. II. EMIL FISCHER and HELMUTH SCHEIBLER (*Ber.*, 1908, **41**, 889—893. Compare Abstr., 1907, i, 192).—*l*-α-Amino*iso*valeric acid (*l*-valin) reacts with nitrosyl bromide yielding an active α-bromo*iso*valeric acid, which with ammonia yields the original valin and not its optical isomeride. This forms another example of the abnormal manner in which compounds containing an *iso*propyl group react (Fischer and Dilthey, Abstr., 1905, i, 35; *Annalen*, 1904, 334). The *α-bromo*iso*valeric* acid crystallises from well-cooled light petroleum in colourless prisms, m. p. 43·5°. In benzene solution it has $[\alpha]_D^{20}$ +22·6°. It is only sparingly soluble in cold water, and has $[\alpha]_D^{20}$ +9·0°. J. J. S.

Synthesis of Polypeptides. XXIII. EMIL FISCHER (*Ber.*, 1908, **41**, 850—864).—Fischer and Abderhalden (Abstr., 1907, i, 737, 990), by the hydrolysis of silk, obtained a soluble tetrapeptide, which is precipitated by ammonium sulphate and is composed of two molecules of glycine and one each of *d*-alanine and *l*-tyrosine. Attempts have now been made to synthesise this compound in the first place by the combination of tyrosine ester with chloroacetyl-*d*-alanylglycine, which led to a tetrapeptide differing from the above in being precipitated by ammonium sulphate with difficulty. In the second place, it was proposed to couple α-bromopropionylglycylglycine with tyrosine, but it was not found possible to obtain the chloride of this tripeptide in a pure state. *dl*-Alanyldiglycylglycine was obtained by coupling the raw product with glycine ester.

d-Bromopropionylglycine, prepared by coupling glycine with *d*-bromopropionyl chloride, crystallises from toluene in long needles, or from water in thin prisms, m. p. 122—123° (corr.), to a colourless liquid. Aqueous ammonia converts it into *d*-alanylglycine,

$$NH_2{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

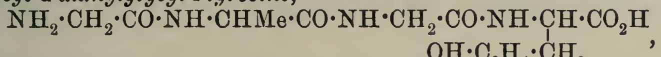
identical with that previously prepared (Abstr., 1905, i, 864). *Chloroacetyl*-d-*alanylglycine* crystallises in microscopic, globular aggregates of minute needles, m. p. 178° (corr. decomp.), and has $[\alpha]_D^{18}$ $-53{\cdot}4°$. *Glycyl*-d-*alanylglycine*,

$$NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

crystallises in very minute needles, which darken at 220°, m. p. 245° (corr. decomp.), and has $[\alpha]_D^{20}$ $-64{\cdot}3°$; it is sparingly soluble in water, and is not precipitated by phosphotungstic acid.

Chloroacetyl-d-*alanylglycyl chloride* is obtained by the action of phosphorus pentachloride and acetyl chloride on the finely-divided substance as a yellow powder. It couples with tyrosine methyl ester in acetone solution to form *chloroacetyl*-d-*alanylglycyl*-l-*tyrosine methyl ester*, which crystallises in faintly yellow, lancet-shaped plates, m. p. 163—164·5° (corr.). The corresponding *acid*, obtained by hydrolysis of the ester with sodium hydroxide, crystallises in colourless, microscopic needles or thin prisms, m. p. 206—207° (corr.); it has an acid reaction, and gives a red coloration with Millon's reagent.

Glycyl-d-*alanylglycyl*-l-*tyrosine*,



$$NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}\underset{OH{\cdot}C_6H_4{\cdot}CH_2}{\underset{|}{CH}}{\cdot}CO_2H,$$

is obtained by the action of ammonia on the above as a colourless, amorphous powder, which decomposes at 229° (corr.) without melting. It has $[\alpha]_D^{20}$ $+4{\cdot}0°$, and shows the biuret coloration and the red coloration with Millon's reagent. It is precipitated by phosphotungstic acid or by tannin, but only with difficulty by ammonium sulphate; it is rapidly hydrolysed by fresh pancreas extract, yielding tyrosine.

Chloroacetyl-d-*alanylglycylglycine ester* forms very minute, matted needles, m. p. 165—167° (corr.). d-*α*-*Bromopropionylglycylglycine*, prepared in the same manner as the antipode (Fischer and Warburg, Abstr., 1905, i, 692), has m. p. 172° (corr.), $[\alpha]_D^{20}$ $+29{\cdot}7°$. d-*Alanylglycylglycine* darkens at 206°, m. p. 220° (corr. decomp.); the antipode behaves similarly, and the m. p., 240° (corr.), previously given (*loc. cit.*) is an error. The tripeptide has $[\alpha]_D^{20}$ $+31{\cdot}3°$, and is easily soluble in water.

α-Bromopropionyldiglycylglycine ethyl ester, prepared by coupling α-bromopropionylglycylglycyl chloride with glycine ethyl ester, crystallises in very minute needles, decomposing at 189° (corr.). On hydrolysis, it yields dl-*α-bromopropionyldiglycylglycine*,

$$CHBrMe{\cdot}CO{\cdot}[NH{\cdot}CH_2{\cdot}CO]_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

which has m. p. 176° (corr.). This acid is more conveniently prepared by coupling diglycylglycine with α-bromopropionyl bromide, when it has m. p. 180° (corr.).

dl-*Alanyldiglycylglycine*,

$$NH_2{\cdot}CHMe{\cdot}CO{\cdot}[NH{\cdot}CH_2{\cdot}CO]_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

formed on treating the above substance with ammonia, becomes brown at 220°, m. p. 242° (corr.). E. F. A.

Conversion of *l*-Serine into the Natural Optically Active Cystine. Emil Fischer and Karl Raske (*Ber.*, 1908, **41**, 893—897). —*dl*-Cystine is obtained when *dl*-*β*-chloro-*α*-aminopropionic acid hydrochloride is heated with water and barium hydrosulphide at 100° for one and a-half hours in sealed tubes, and the resulting product oxidised by atmospheric oxygen in the presence of ammonia (Erlenmeyer, Abstr., 1903, i, 792). When the optically active natural serine is used, an active cystine is obtained which is identical with the cystine from natural sources. The conclusion is drawn that natural cystine, serine, and alanine belong to the same genetic group. The configurations previously suggested for the last two compounds (Abstr., 1907, i, 393) cannot be regarded as rigidly established.

Full details for the preparation of barium hydrosulphide are given.
J. J. S.

Preparations of Sodium Glycocholate. William C. M. Lewis (*Bio-Chem. J.*, 1908, 3, 119—128).—Strecker's formula for sodium glycocholate is confirmed. The ordinary methods of extraction of mixed bile salts do not yield a product consisting entirely of sodium glycocholate and taurocholate, but there is in addition a varying amount of sodium salts of fatty acids of much smaller molecular weight. This admixture may amount to as much as 50% of the total product. It is suggested that sodium myristate is the principal component of this admixture.
W. D. H.

A New Method of Forming *iso*Cyanates [Carbimides]. I. Richard Anschütz (*Annalen*, 1908, 359, 202—216. Compare Freund and Asbrand, Abstr., 1895, i, 576).—An application of Hofmann's synthesis of thiocarbimides from carbon disulphide and primary amines to the formation of carbimides from carbonyl sulphide.

The action of primary amines on carbonyl sulphide leads to the formation of alkylammonium alkylthiolcarbamates, $NHR\cdot CO\cdot S\cdot NH_3R$, which react with metallic salts in aqueous or aqueous-acetone solution, forming the metallic alkylthiocarbamates. As Hofmann's method of decomposing the metallic alkyldithiocarbamates in aqueous solution is inapplicable to the formation of carbimides, which react with water forming carbon dioxide and *s*-dialkylcarbamides, the author has studied the action of heat on the metallic salts of alkyldithio- and alkylthiocarbamates, and finds that, whilst mercuric ethyldithiocarbamate decomposes at 150—160° forming only small amounts of ethyl thiocarbimide together with carbon disulphide, *s*-diethylcarbamide, and considerable quantities of mercuric sulphide, mercuric alkylthiolcarbamates, $(NHR\cdot CO\cdot S)_2Hg$, when heated, yield mercuric sulphide, carbonyl sulphide, and *s*-dialkylcarbamides together with small amounts of the carbimides, but the chloromercuric salts,

$$NHR\cdot CO\cdot S\cdot HgCl,$$

decompose chiefly into mercuric sulphide, hydrogen chloride, and alkylcarbimides, the formation of carbonyl sulphide and the *s*-dialkylcarbamide taking place in this case to only a small extent. The decomposition of the mercuric alkylthiolcarbamates is considered to take place probably in two stages, the first leading to the formation of mercuric sulphide and the intermediate product, $S(CO\cdot NHR)_2$.

Ethylammonium ethylthiolcarbamate, $C_5H_{14}ON_2S$, prepared by passing carbonyl sulphide into an ethereal solution of ethylamine, crystallises in white needles, m. p. 88—89°, is hygroscopic, decomposes in contact with water, forming hydrogen sulphide and an *oil*, and yields the mercuric and chloromercuric salts as white precipitates on addition of the calculated quantities of mercuric chloride to its concentrated aqueous solution. *Mercuric ethylthiolcarbamate*, $(C_3H_6ONS)_2Hg$, has an odour of ethyl carbimide when moist or after drying; it commences to decompose at 90°, evolving carbonyl sulphide, and at 156—160° yields red mercuric sulphide, *s*-diethylcarbamide, and small amounts of ethylcarbimide. The *chloromercuric* salt, $C_3H_6ONClHg$, has an odour of ethylcarbimide, yields *s*-diethylcarbamide when boiled with water, and forms ethylcarbimide when heated. The *silver*, *copper*, and *lead* salts of ethylthiolcarbamic acid were also prepared.

iso*Butylammonium* iso*butylthiolcarbamate*, $C_9H_{22}ON_2S$, crystallises in glistening leaflets, m. p. 102°, and is more stable than the ethyl compound. The *mercuric* and *chloromercuric* salts behave in the same manner as those of the ethyl compound. *iso*Butylcarbimide (Brauner, Abstr., 1880, 228) is a colourless liquid, b. p. 101·5°/760 mm., has an odour resembling that of ethylcarbimide, and reacts with *iso*butylamine, forming *s*-di*iso*butylcarbamide. The *copper*, $C_{10}H_{20}O_2N_2S_2Cu$, and *cadmium*, $C_{10}H_{20}O_2N_2S_2Cd$, salts were analysed; when heated, these salts yield *s*-di*iso*butylcarbamide. G. Y.

Nitroacetonitrile. III. WILHELM STEINKOPF and LUDWIG BOHRMANN (*Ber.*, 1908, **41**, 1044—1052).—After many unsuccessful attempts (compare Abstr., 1907, i, 490), nitroacetonitrile has at last been prepared by treating methazonic acid with thionyl chloride in ether. That the compound so obtained is nitroacetonitrile follows from the fact that it yields α-nitroethenylamino-oxime with hydroxylamine, and gives the nitrolic acid reaction and Konowaloff's reaction. Its formation from methazonic acid proves the correctness of the formula assigned to this substance by Meister (Abstr., 1907, i, 885). Further, since the compound obtained by Steiner (Trans., 1876, ii, 288) from fulminuric acid, and described by him as nitroacetonitrile, is not identical with nitroacetonitrile, this author's formulation of fulminuric acid as nitrocyanoacetamide becomes doubtful. Attempts are being made to prepare nitrocyanoacetamide.

Nitroacetonitrile, $NO_2\cdot CH_2\cdot CN$, is obtained as a fairly stable, yellow, limpid oil; when pure, it may be distilled under reduced pressure, b. p. 96°/14 mm.; it is not explosive, neither is the *ammonium* salt, which crystallises in slender, yellowish-white needles, decomposing at 130—135°; the *silver* salt, obtained as a brown precipitate, is, however, very explosive. An aqueous solution of the ammonium salt when treated with a solution of diazobenzene nitrate yields *nitrocyanoformaldehydephenylhydrazone*, $CN\cdot C(NO_2):N\cdot NHPh$; it forms glistening, reddish-brown crystals, decomposing at 108°, and is soluble in dilute alkalis.

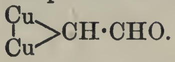
α-*Nitroethenylamino-oxime*, $NO_2\cdot CH_2\cdot C(NH_2):NOH$, obtained by the action of hydroxylamine on nitroacetonitrile, forms yellow crystals and decomposes suddenly at 108°. *Dibromonitroacetonitrile*,

$$NO_2\cdot CBr_2\cdot CN,$$

prepared by adding bromine to an aqueous solution of ammonium nitroacetonitrile, is a pale yellow oil, b. p. 57—58°/12 mm., with an unpleasant odour; it solidifies to a crystalline mass at about $-30°$.

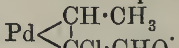
When nitroacetamide or its ammonium salt is warmed with thionyl chloride, it is converted into a compound which is probably *nitroacetimide chloride*, $NO_2 \cdot CH_2 \cdot CCl{:}NH$; it crystallises from water in white crystals with H_2O; the anhydrous substance has m. p. 157—158°. When boiled with water for some time, it is converted into a *substance*, $C_2H_4O_3N_2$, decomposing violently at 121°. The nature of this compound is under investigation. W. H. G.

Metallic Acetylene Compounds. OSKAR MAKOWKA (*Ber.*, 1908, 41, 824—829. Compare Abstr., 1907, ii, 399, 403).—The copper acetylene compound, obtained by the precipitation of a cuprous salt by acetylene, is of constant composition, $C_2H_2OCu_2$, whether derived from chloride, nitrate, sulphate or acetate, or by precipitation in acetone solution. When oxidised with hydrogen peroxide, volatile products, showing an aldehyde reaction, are formed. In view of this, the compound is regarded as dicuproacetaldehyde of the constitution



$$\begin{matrix}Cu\\|\\Cu\end{matrix}\!>CH \cdot CHO.$$

The so-called palladium acetylene has the formula C_4H_5OClPd. It is non-explosive, and yields palladium when ignited. When heated with water or alkali hydroxides, butyraldehyde is produced, and, on fusion with potassium hydroxide, butyric acid and possibly also higher fatty acids are formed. The compound is considered to be palladochlorobutyraldehyde,



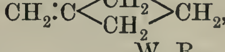
$$Pd\!<\!\begin{matrix}CH \cdot CH_3\\|\\CCl \cdot CHO\end{matrix}.$$

E. F. A.

The Study of Hydro-aromatic Substances. EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1907, 77, 104—115).—This report deals with the action of reducing agents on 5-chloro-3-keto-1 : 1-dimethyl-Δ^4-tetrahydrobenzene; the action of alcoholic potassium hydroxide on 3-bromo-1 : 1-dimethylhexahydrobenzene; recent work on hydroaromatic hydrocarbons, alcohols, ketones, and acids; steric hindrance in the formation of rings; optical influence of conjugated unsaturated groups, and velocity of chemical change in the polymethylene series. T. H. P.

Products of the Action of Aluminium Chloride and Hydrogen Chloride on Benzene; Phenylmethyl*cyclo*pentane. GABRIEL GUSTAVSON (*Compt. rend.*, 1908, 146, 640—642).—When a mixture of benzene and aluminium chloride saturated with hydrogen chloride is heated for some hours in hermetically sealed flasks on a water-bath, a dark brown liquid gradually separates, which on decomposition by water gives a mixture of benzene, hydrocarbons, b. p. up to 360°, and a resinous residue (*J. Russ. Phys. Chem. Soc.*, 1878, 10, 390). By treating the fraction b. p. 230—240° with fuming sulphuric acid and heating the sulphonic acid, isolated through its barium salt, with hydrochloric acid in sealed tubes at 180—200°, the author has obtained a hydrocarbon, $C_{12}H_{16}$, b. p. 230—232°,

n_4^{16} 1·5210, apparently identical with the 3-phenyl-1-methyl*cyclo*pentane described by Borsche and Menz (this vol., i, 149). It is not attacked by bromine, and not immediately by potassium permanganate solution. On oxidation by the latter or by chromic acid at 100°, benzoic and acetic acids are formed. When the dark brown liquid is extracted with light petroleum, a substance remains which will again combine with benzene, and the product on saturation with hydrogen chloride gives more phenylmethyl*cyclo*pentane mixed with more highly phenylated cyclic hydrocarbons. Amongst the latter, Kursanoff's diphenyl*cyclo*hexane (Abstr., 1902, i, 20) has been detected. Probably the *cyclo*hexane is transformed into the methyl*cyclo*pentane, and the toluene observed by Friedel and Crafts arises from a transposition of the latter. E. H.

Transformations and New Nitrogenous Derivatives of Vinyltrimethylene. NICOLAUS J. DEMJANOFF (*Ber.*, 1908, 41, 915—920).—The constitution of Gustavson's vinyltrimethylene not having yet been finally established (compare Abstr., 1896, i, 699; Fecht, Abstr., 1907, i, 906), the action of nitrogen trioxide on the hydrocarbon was investigated, and by the reduction of the additive product so obtained *cyclo*butanone was formed. The *nitrosite*, $C_5H_8O_3N_2$, separates from an ethereal solution at 0° when the gas from arsenious oxide and nitric acid (D 1·36) is passed through it, and forms colourless, glistening leaflets, m. p. 145° to a deep blue liquid. A good yield of succinic acid is obtained by its oxidation with concentrated nitric acid. It is shown to be a ψ-nitrosite by its conversion into the weak *base*, $NO_2{\cdot}C_5H_8{\cdot}NHPh$, by aniline, nitrous oxide being liberated; this forms yellow leaflets, m. p. 98°; the *hydrochloride*, $C_{11}H_{15}O_2N_2Cl$, is crystalline. Reduction of the nitrosite with tin and hydrochloric acid, as well as of the liquid product obtained simultaneously with the nitrosite, leads to the formation of a *diamine*, a colourless liquid, b. p. 180—185°. The *dihydrochloride*, $C_5H_8(NH_2,HCl)_2$ forms colourless prisms; the *platinichloride*, $C_5H_{12}N_2,H_2PtCl_6,3H_2O$, orange-red prisms; the *aurichloride*, $C_5H_{12}N_2,2HAuCl_4,H_2O$, yellow leaflets, and the *picrate*, $C_5H_8(NH_2)_2,2C_6H_2(NO_2)_3{\cdot}OH$, needles. These results show that in the nitrosite and liquid product the nitrogen atoms are directly united to carbon. In addition to the diamine a neutral product was obtained possessing aldehydic properties, b. p. 98—101°; the semicarbazone has m. p. 201—202°, and it is therefore identified as *cyclo*butanone, the formation of which is most easily explained by assuming the hydrocarbon to be methylene-*cyclo*butane,  $CH_2{:}C{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CH_2$, but the question requires further investigation. W. R.

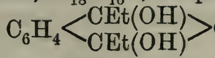
Action of Nitric Acid on Saturated Hydrocarbons. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 184—192. Compare Konowaloff, Abstr., 1907, i, 1).—The formation of nitro-compounds is only the first stage in the action of nitric acid on hydrocarbons, and consequently the mass of the nitric acid employed influences greatly the final products obtained; thus, if the quantity of acid is small, only nitro-compounds are obtained, but if the acid is increased, oxidation products are formed and the proportion of the nitro-compounds is diminished.

The nitration of hexahydro-ψ-cumene, b. p. 142—144°, can be carried out with equally good results, and more conveniently in open vessels than in sealed tubes if 75—150 c.c. of nitric acid, D 1·3, are used for 100 c.c. of the hydrocarbon, the chief products being mononitro-derivatives. Z. K.

The Study of Isomorphous Derivatives of Benzenesulphonic Acid. Henry A. Miers, Henry E. Armstrong, W. Palmer Wynne, and William J. Pope (*Brit. Assoc. Report*, 1907, 77, 272).—All the possible isomeric sulphonic chlorides and sulphonic bromides of the isomeric dichloro-, the isomeric dibromo-, and the isomeric chlorobromobenzenes are to be prepared and examined crystallographically so as to determine the extent of variation in the series of closely-related compounds. T. H. P.

Catalytic Reactions at High Temperatures and Pressures. XV. Reduction of Anthracene and Phenanthrene in Presence of Nickel Oxide. Wladimir N. Ipatieff, W. Jakowieff, and L. Rakitin (*Ber.*, 1908, 41, 996—1000. Compare Godchot, Abstr., 1904, i, 987; 1906, i, 76; Schmidt and Mezger, Abstr., 1907, i, 1022).—When repeatedly heated with hydrogen in presence of nickel oxide at 260—270°/100—125 atmospheres for ten to fifteen hours, anthracene is reduced in three stages. The product of the first heating consists chiefly of tetrahydroanthracene; this is reduced in the second stage to decahydroanthracene, $C_{14}H_{20}$, which crystallises in odourless plates, m. p. 73—74° (52—53°: Lucas, Abstr., 1888, 1201), and when again reduced yields a mixture of perhydroanthracene and a *substance*, m. p. $-3°$, having apparently the same composition. The yields are not quantitative, as part of the anthracene decomposes, forming carbon and methane.

The reduction of phenanthrene takes place in three stages in the same manner, but at higher temperatures. The reduction products are obtained in quantitative yields, as even at 400° carbon and methane are not formed. The product of the first stage is a mixture of dihydro- and tetrahydro-phenanthrene, and yields two *picrates*, m. p. 135—137°, and orange-red needles, m. p. 105—106°, respectively. The second reaction product, m. p. $-4°$ to $-5°$, is octahydrophenanthrene, perhaps containing other hydrocarbons. The final reduction product consists of perhydrophenanthrene, $C_{14}H_{24}$, which is a colourless liquid, b. p. 266—276°, has an odour resembling caoutchouc, becomes slightly yellow on prolonged exposure to light, and is not attacked by nitric acid, bromine, or potassium permanganate at the ordinary temperature. G. Y.

Derivatives of Dihydroanthracene. Latham Clarke (*Ber.*, 1908, 41, 935—936).—The reaction between anthraquinone and magnesium ethyl bromide in ethereal solution leads to the formation of a *substance*, $C_{18}H_{16}O$, m. p. 159°, and of *dihydroxydiethyldihydroanthracene*,  $C_6H_4<\begin{smallmatrix}CEt(OH)\\CEt(OH)\end{smallmatrix}>C_6H_4$, m. p. 175°, which separates from ether in large, greenish-white needles containing 1 mol. of ether, and from alcohol in thick, white plates, which also contain alcohol of crystallisation, which is rapidly lost by exposure to the air. C. S.

Fluorene Perhydride. LEOPOLD SPIEGEL (*Ber.*, 1908, 41, 884—886).—A repetition of the experiments of the author and Liebermann (Abstr., 1889, 719) shows that, contrary to the statement of Schmidt and Mezger (this vol., i, 16), fluorene perhydride, $C_{13}H_{22}$, is actually existent. C. S.

Attempt to Prepare Hexaphenylethane. RICHARD ANSCHÜTZ (*Annalen*, 1908, **359**, 196—201).—It was observed previously (Trans., 1885, **47**, 898, 899) that phenyl fumarate, when heated, decomposes in two stages into carbon dioxide and stilbene, the intermediate product being phenyl cinnamate. Recently, Tschitschibabin has drawn attention to the instability of carboxyl and cyano-groups when attached to the same carbon atom as other negative groups (Abstr., 1907, i, 27). These facts, together with the long-known formation of triphenylmethane by the decomposition of triphenylacetic acid, induced the author to study the action of heat on triphenylmethyl triphenylacetate, $CPh_2\cdot CO_2\cdot CPh_3$, triphenylmethyl fumarate,

$$CPh_3\cdot CO_2\cdot CH\colon CH\cdot CO_2\cdot CPh_3,$$

and phenyl triphenylacetate, $CPh_3\cdot CO_2Ph$, as these might be expected, in analogy with the formation of stilbene and triphenylmethane, to yield hexaphenylethane, *s*-bistriphenylmethylethylene, and tetraphenylethane respectively. Only in the case of the first of these esters, however, has any indication of the formation of such a product been obtained.

Triphenylmethyl triphenylacetate, $C_{39}H_{30}O_2$, prepared by the action of triphenylmethyl chloride on silver triphenylacetate in boiling benzene solution, crystallises in needles, m. p. 184—185°, is readily hydrolysed by alkalis, forming triphenylcarbinol and triphenylacetic acid, and, when heated at 185—200° in a vacuum, loses carbon dioxide and yields triphenylmethane, a white, crystalline *substance*, soluble in chloroform, a *product*, m. p. about 210°, insoluble in chloroform, but soluble in benzene, and an amorphous *residue*, m. p. about 300°, which dissolves in boiling ethylene dibromide and may be *hexaphenylethane*, $C_{38}H_{30}$.

Phenyl triphenylacetate, $C_{26}H_{20}O_2$, prepared from sodium phenoxide and triphenylacetyl chloride, crystallises in small needles, m. p. 122°, and when heated above its m. p. loses carbon dioxide and forms triphenylmethane and phenol.

Triphenylmethyl fumarate, $C_{42}H_{32}O_4$, prepared from triphenylmethyl chloride and silver fumarate, crystallises from carbon tetrachloride in needles containing CCl_4, which is lost at 100°; m. p. 152—153°. At 200°, the ester loses carbon dioxide, forming a mixture from which a pure product has not yet been obtained. G. Y.

Catalytic Reactions at High Temperatures and Pressures. XIII. Reduction of Aromatic Amines and Quinoline in Presence of Nickel Oxide. Wladimir N. Ipatieff (*Ber.*, 1908, **41**, 991—993. Compare Abstr., 1907, i, 828).—Whilst the action of hydrogen on aromatic amines in presence of nickel oxide under the atmospheric pressure leads to the formation of large amounts of abnormal products, sometimes, as in the case of quinoline, even to the complete suppression of the normal reduction product (Padoa and Carughi, Abstr., 1906, i, 765), the reduction by means of hydrogen in presence of nickel oxide at high temperatures and under high pressures takes place more simply. When heated with hydrogen in presence of nickel oxide at 220—230°/115—120 atmospheres for forty to fifty hours, aniline forms amino*cyclo*hexane in a 40—50% yield, together with di*cyclo*hexylamine and phenyl*cyclo*hexylamine in 10% yields. Under similar conditions, diphenylamine yields di*cyclo*hexylamine and traces of *cyclo*hexylamine, whilst quinoline is reduced almost quantitatively to decahydroquinoline, or, on less prolonged heating, to tetrahydroquinoline. G. Y.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. Frederic S. Kipping, Kennedy J. P. Orton, Siegfried Ruhemann, Arthur Lapworth, and John T. Hewitt (*Brit. Assoc. Report*, 1907, **77**, 101—103).—A detailed study of the conditions governing the transformation of 2 : 4-dichloro-1-nitroaminobenzene into the isomeric 2 : 4-dichloro-6-nitroaniline and a study of the wandering of bromine in the chlorination of bromo-anilines.

T. H. P.

Preparation of *p*-Toluidine from Mixed Toluidines by means of *p*-Toluidine Hydrate. Richard J. Friswell (*J. Soc. Chem. Ind*, 1908, **27**, 258).—Referring to the recent publication of Walker and Beveridge (Trans., 1907, 91, 1797), the author calls attention to the fact that, in 1889, he devised the mode of separating *p*-toluidine from mixed toluidines by means of *p*-toluidine hydrate, and successfully carried it out on a large scale. Technical details are given in the original. J. V. E.

Condensation of Chloral with Primary Aromatic Amines. II. Alvin S. Wheeler (*J. Amer. Chem. Soc.*, 1908, **30**, 136—142).—In an earlier paper (Wheeler and Weller, Abstr., 1903, i, 246), it was stated that chloral condenses with *o*- and *p*-nitroanilines to form trichloroethylidenedi-*o*- and -*p*-nitro-anilines.

An account is now given of the behaviour of chloral with other primary arylamines. The products crystallise well, and are decomposed by strong mineral acids with regeneration of the amine. They react readily with bromine at the ordinary temperature to form bromo-derivatives, in which the bromine atom probably replaces the hydrogen of the chloral residue.

[With C. W. Miller.]—*Trichloroethylidenedi*-p-*bromoaniline*,

$$CCl_3\cdot CH(NH\cdot C_6H_4Br)_2,$$

m. p. 140°, forms colourless needles and decomposes at 205°. The *bromo*-derivative, m. p. 203°, crystallises in colourless plates, and the *chloro*-derivative, m. p. 93°, in long needles.

[With W. S. Dickson.]—*Trichloroethylidenedi*-o-*methoxyphenylamine*, $CCl_3·CH(NH·C_6H_4·OMe)_2$, m. p. 121°, forms large, pale yellow, rhombohedra or long, slender prisms, and is soluble in 100 c.c. of alcohol to the extent of 7 grams at the b. p. and 2·5 grams at 25°. The *bromo*-derivative crystallises in clusters of needles, and decomposes at about 230°.

Trichloroethylidenedi-p-*methoxyphenylamine*, m. p. 118—120°, forms brilliant, pink scales, and decomposes at 158°. By the action of bromine, a *compound* is obtained which blackens at about 198°.

[With W. S. Dickson.]—Trichloroethylidene-*o*-aminobenzoic acid (chloral-anthranilic acid) (Niementowski and Orzechowski, Abstr., 1896, i, 187), m. p. 152°, yields a *bromo*-derivative decomposing at 237°. When trichloroethylidenedi-*o*-aminobenzoic acid (chloral-dianthranilic acid) (Niementowski, Abstr., 1903, i, 91) is boiled with acetic anhydride, *o*-acetylaminobenzoic acid is produced. The *bromo*-derivative of chloral-dianthranilic acid has m. p. 236° (decomp.).

[With Strowd Jordan.]—*Trichloroethylidenedi*-o-*tolylamine*,

$$CCl_3·CH(NH·C_6H_4Me)_2,$$

m. p. 80°, forms silky needles, and yields a *bromo*-derivative, m. p. about 268°. Physiologically, the compound produces a numbing effect. E. G.

Condensation Products of Dibromo-*p*-hydroxybenzyl Bromide with Aromatic Bases. Karl Auwers and Alfred Dombrowski (*Ber.*, 1908, 41, 1053—1058).—A further contribution to the study of the influence of the position of the methyl group on the chemical properties of benzenoid compounds (compare Auwers, Abstr., 1906, i, 258).

Although derivatives of dibromo-*p*-hydroxy-ψ-cumylaniline are readily obtained by the action of dibromo-*p*-hydroxy-ψ-cumyl bromide on an aromatic base in ethereal solution (compare Auwers and Dombrowski, Abstr., 1906, i, 380), it is found that when dibromo-*p*-hydroxybenzyl bromide acts on aniline, *p*-toluidine, or *m*-toluidine, instead of the expected substituted benzylaniline, the corresponding benzylidene derivative is obtained. However, the normal reaction product is obtained when *o*-toluidine, ψ-cumidine, *p*-xylidine, or *as*-*m*-xylidine is employed. It is therefore evident that the presence of the methyl group ortho to the amino-group prevents the oxidation of the substituted benzylaniline to the corresponding benzylidene derivative; further, since benzylidene derivatives have never been obtained when dibromo-*p*-hydroxy-ψ-cumyl bromide is employed, it follows that the same protective influence against oxidation is exerted by the methyl group when ortho to the $-CH_2Br$ group.

The nature of the solvent employed also influences the course of the reaction. Only in ethereal solution does the reaction take place in the manner above described; when benzene is used, the chief product formed, for example, by the action of dibromo-*p*-hydroxybenzyl bromide on *p*-toluidine, is the di-derivative,

$$C_6H_4Me·N(CH_2·C_6H_2Br_2·OH)_2.$$

The benzylidene derivatives obtained by the action of dibromo-*p*-hydroxybenzyl bromide on aniline and *p*-toluidine were identical with those described by Paal and Kromschröder (Abstr., 1896, i, 225); the m. p. of the *p*-toluidine derivative,

$$OH\cdot C_6H_2Br_2\cdot CH:N\cdot C_6H_4Me,Et\cdot OH,$$

was found to be 187°, and not 157° as stated by these authors.

The following new compounds were prepared: *dibromo*-p-*hydroxybenzylidene*-m-*toluidine*, $C_{14}H_{11}ONBr_2$, a dark red, crystalline powder, m. p. 155·5—157°; *dibromo*-p-*hydroxybenzyl*-o-*toluidine*, $C_{14}H_{13}ONBr_2$, a white, crystalline powder, m. p. 117·5—119°; the N-*acetate*,

$$C_{16}H_{15}O_2NBr_2,$$

forms needle-shaped crystals; *dibromo*-p-*hydroxybenzyl*-as-m-*xylidine* N-*acetate*, $C_{17}H_{17}O_2NBr_2$, crystallises in very small leaflets, m. p. 175°; the isomeric *p*-xylidine compound forms colourless crystals, m. p. 240—241°; *dibromo*-p-*hydroxybenzylidene*-as-m-*xylidine*, $C_{15}H_{13}ONBr_2$, is a red powder, m. p. 161°; *dibromo*-p-*hydroxybenzyl*-ψ-*cumidine*,

$$C_{16}H_{17}ONBr_2,$$

crystallises in slender needles, m. p. 123—125°; the N-*acetate* has m. p. 205°; *bisdibromo*-p-*hydroxybenzyl*-p-*toluidine*,

$$C_6H_4Me\cdot N(CH_2\cdot C_6H_2Br_2\cdot OH)_2,$$

has m. p. 134—135°; *tetrabromo*-p-*hydroxybenzylaniline*, $C_{13}H_9ONBr_4$, crystallises in small, glistening, pearly leaflets, m. p. 126—127°; when its alcoholic solution is boiled for some time, it is partly converted into *bistetrabromo*-p-*hydroxybenzylaniline*,

$$C_6H_5\cdot N(CH_2\cdot C_6Br_4\cdot OH)_2,$$

a fine powder, m. p. 212°. W. H. G.

Asymmetric Nitrogen. XXXII. Dependence of the Velocity of Racemisation of Optically Active Ammonium Salts on the Nature of the Anion. Edgar Wedekind, Otto Wedekind, and F. Paschke (*Ber.*, 1908, **41**, 1029—1035. Compare E. Wedekind, Abstr., 1906, i, 161, 419).—The velocities with which *d*-phenylbenzylmethylpropylammonium iodide, bromide, and chloride undergo autoracemisation in chloroform solution at 35° have been measured, the velocity constants obtained being, for the iodide, $K = 0·0065$, for the bromide, $K = 0·0013$, and for the chloride, $K = 0·00027$, that is, in the ratio Cl : Br : I = 1 : 5 : 25. The rate of change of the bromide in bromoform solution was found to be the same as in chloroform solution.

Similar comparative measurements were made with *d*-phenylbenzylmethylallylammonium bromide and iodide in chloroform solution at 25°, 35°, and 45°, the K values obtained being, for the iodide, 0·0012 and 0·0040 at 25° and 35° respectively, and for the bromide, 0·00061 and 0·0024 at 35° and 45° respectively. From these values, it is seen that (1) the iodide undergoes racemisation about six times more rapidly than the bromide at the same temperature (35°); (2) the allylammonium salts are more stable than the corresponding propyl salts.

The effect of an increase in temperature on the rate of change is in several cases quite abnormal; for example, the K values for *d*-phenylbenzylmethylpropylammonium iodide at 25° and 35° are respectively 0·0013 and 0·0065.

l-*Phenylbenzylmethylpropylammonium chloride* has been prepared; it forms small, colourless crystals decomposing at 174—175°, $[\alpha]_D - 143·8°$ (in chloroform). W. H. G.

Phenyl Mesaconates. ROSALIND CLARKE (*Annalen*, 1908, **359**, 188—195).—The esters described in this paper were prepared in amplification of Anschütz's study of derivatives of mesaconic acid (Abstr., 1907, i, 468).

Phenyl mesaconate, $CO_2Ph·CH:CMe·CO_2Ph$, prepared by the action of mesaconyl chloride on sodium phenoxide in boiling toluene solution, crystallises from carbon disulphide in yellow leaflets, m. p. 66—67°; it resembles phenyl fumarate in that it evolves carbon dioxide when heated at high temperatures. On hydrolysis with 1 mol. of potassium hydroxide in boiling aqueous-acetone solution, it yields *α-phenyl hydrogen mesaconate*, $CO_2Ph·CH:CMe·CO_2H$, which crystallises from light petroleum in needles, m. p. 99°. *α-Phenyl β-methyl mesaconate*, $CO_2Ph·CH:CMe·CO_2Me$, m. p. 45—46°, b. p. 166°/13 mm., is obtained by gently heating sodium phenoxide with β-methyl mesaconyl α-chloride in ethereal solution.

β-Phenyl hydrogen mesaconate could not be obtained by partial esterification of the acid, but the *β-phenyl α-methyl* ester,

$$CO_2Me·CH:CMe·CO_2Ph,$$

m. p. 23—25°, b. p. 176°/20 mm., is formed from sodium phenoxide and α-methyl mesaconyl β-chloride.

α-Phenyl mesaconyl β-chloride, $CO_2Ph·CH:CMe·COCl$, obtained as a crystalline mass on treatment of the α-phenyl hydrogen ester with phosphorus pentachloride in chloroform solution and distillation of the phosphoryl chloride and the solvent in a vacuum, yields the following three substances when treated with the corresponding bases in ethereal solution. *α-Phenyl mesacon-β-amate*, $CO_2Ph·CH:CMe·CO·NH_2$, crystallises from ether in white needles, m. p. 114—115°. *α-Phenyl mesacon-β-anilate*, $CO_2Ph·CH:CMe·CO·NHPh$, white needles, m. p. 121°. *α-Phenyl mesacon-β-*p*-toluidate*, $CO_2Ph·CH:CMe·CO·NH·C_6H_4Me$, yellow needles, m. p. 129—130°.

β-Phenyl mesacon-α-anilate, white crystals, m. p. 114—115°, and the corresponding *α-*p*-toluidate*, yellow needles, m. p. 122°, are prepared by the action of mesacon-α-anilyl and mesacon-α-*p*-toluidyl chlorides on sodium phenoxide.

Whilst the β-alkyl mesacon-α-anilates and -α-*p*-toluidates melt at the same temperatures as, or at higher temperatures than, the corresponding β-anilates and β-*p*-toluidates, the α-phenyl mesacon-β-anilate and β-*p*-toluidate melt 7° higher than their isomerides. G. Y.

2:4:6-Trichlorophenol and its Transformation into Chlorinated Benzoquinones. EUGÈNE LÉGER (*Compt. rend.*, 1908, **146**, 694—697).—2:4:6-Trichlorophenol can be prepared readily and in quantity when concentrated eau de Javel is used instead of the dilute solution of hypochlorite employed by Chandelon (Abstr., 1883, 1108). It has m. p. 66—67° (corr.) [Chandelon (*loc. cit.*) gives 54°].

By the action of nitric acid, D 1·41, containing a small quantity of hydrochloric acid, trichlorophenol is converted into a mixture of tri- and tetra-chlorobenzoquinones, which can be separated by fractional crystallisation from alcohol; trichlorobenzoquinone softens at 166° and melts at 168° (corr.) (Graebe gives 164—166°, *Annalen*, 1868, **146**, 1).

M. A. W.

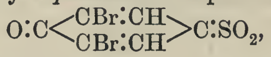
Basic Tri-iodophenoxide of Bismuth. Oreste Carrasco (*Boll. chim. farm.*, 1908, **47**, 109—112).—The author gives an improved method for preparing 2 : 4 : 6-tri-iodophenol (compare Brenans, Abstr., 1901, i, 322), from which he obtains a basic bismuth derivative possessed of therapeutic value.

By adding a potassium iodide solution of rather more iodine than is required by the equation $C_6H_5{\cdot}OH + 3KHO + 6I = C_6H_2I_3{\cdot}OH + 3KI + 3H_2O$ gradually to a solution of phenol in a large excess of potassium hydroxide (8 mols.) solution, a theoretical yield of 2 : 4 : 6-tri-iodophenol, free from di- or mono-iodophenol, is obtained.

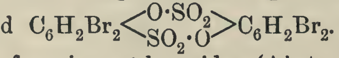
Monohydrated bismuthyl 2 : 4 : 6-*tri-iodophenoxide*, $C_6H_2I_3{\cdot}O{\cdot}Bi(OH)_2$, prepared by treating a solution of 2 : 4 : 6-tri-iodophenol (1 mol.) in alkali with a solution of bismuth nitrate (rather less than 1 mol.) in 45% aqueous glycerol, is obtained as a heavy, yellow, amorphous powder. The corresponding *anhydrous* derivative, $C_6H_2I_3{\cdot}O{\cdot}BiO$, to which the name 'neoform' is given, is a yellow powder having a faint odour recalling that of xeroform, a similar compound containing bromine in place of iodine; it begins to decompose at 170—180°.

T. H. P.

Quinonoid Sulpho-derivatives. Theodor Zincke and R. Brune (*Ber.*, 1908, **41**, 902—905).—An acetone solution of 2 : 6-dibromophenol-4-sulphonyl chloride (Abstr., 1907, i, 698) becomes deep yellow when shaken with sodium acetate solution. Hydrogen chloride is eliminated, and probably a *quinonoid* compound,



$$O{:}C{<}\begin{matrix}CBr{:}CH\\CBr{:}CH\end{matrix}{>}C{:}SO_2,$$

is formed. This compound has not been isolated, as the solution rapidly becomes colourless and deposits a colourless, crystalline compound, having the same composition, and probably representing the polymeric compound  $C_6H_2Br_2{<}\begin{matrix}O{\cdot}SO_2\\SO_2{\cdot}O\end{matrix}{>}C_6H_2Br_2$. This behaviour is analogous to that of various ψ-bromides (Abstr., 1907, i, 125). The polymeride readily reacts with methyl or ethyl alcohol and also with aniline, yielding the same derivatives as are formed when these substances react with the original sulphonyl chloride.

The polymeride is practically insoluble in the ordinary organic solvents, crystallises from hot nitrobenzene in rhombic plates and prisms, and is not readily oxidised.

Methyl 2 : 6-*dibromophenol*-4-*sulphonate*,

$$OH{\cdot}C_6H_2Br_2{\cdot}SO_2{\cdot}OMe,$$

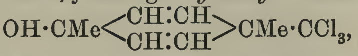
crystallises from benzene in rhombic plates, m. p. 196—197°, which dissolve readily in alkalis. The corresponding *ethyl* ester,

$$C_8H_8O_4SBr_2,$$

crystallises in prisms, m. p. 146—147°. The *sulphanilide*,

$OH\cdot C_6H_2Br_2\cdot SO_2\cdot NHPh$,

crystallises in colourless plates, m. p. 177°. J. J. S.

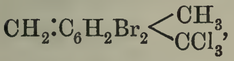
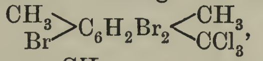
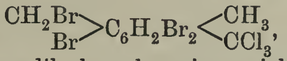
4-Hydroxy-1 : 4-dimethyl-1-trichloromethyldihydrobenzene. THEODOR ZINCKE and FR. SCHWABE (*Ber.*, 1908, **41**, 897—902).—Zincke and Suhl's ketone, $C_8H_7OCl_3$ (Abstr., 1907, i, 37), reacts readily with magnesium methyl iodide, yielding 4-*hydroxy*-1 : 4-*dimethyl*-1-*trichloromethyl*cyclo*hexadiene*,  $OH\cdot CMe<\begin{matrix}CH:CH\\CH:CH\end{matrix}>CMe\cdot CCl_3$, which crystallises from light petroleum in slender needles or plates, m. p. 131—132°. It is extremely unstable, and, when kept, rapidly gives up water, yielding 1-*methyl*-4-β-*trichloroethylbenzene*,

$C_6H_4Me\cdot CH_2\cdot CCl_3$,

which crystallises from methyl alcohol in slender plates, m. p. 31—33°. When oxidised, this compound yields terephthalic acid, and when heated with alcoholic potash, gives 1-*methyl*-4-β-*dichlorovinylbenzene*,

$C_6H_4Me\cdot CH:CCl_2$,

colourless plates, m. p. 40—41°.

The carbinol reacts with a chloroform solution of bromine, yielding bromo-derivatives which probably have the following constitution:  $CH_2:C_6H_2Br_2<\begin{matrix}CH_3\\CCl_3\end{matrix}$, m. p. 90—91°;  $\begin{matrix}CH_3\\Br\end{matrix}>C_6H_2Br_2<\begin{matrix}CH_3\\CCl_3\end{matrix}$, m. p. 106—107° (decomp.), and  $\begin{matrix}CH_2Br\\Br\end{matrix}>C_6H_2Br_2<\begin{matrix}CH_3\\CCl_3\end{matrix}$, m. p. 133° (decomp.). The latter two readily lose bromine, yielding the dibromo-derivative. J. J. S.

Action of Chlorine on Dithymol. HENRI COUSIN (*Compt. rend.* 1908, **146**, 636—637. Compare this vol., i, 84, 162).—When dithymol (1 mol.), suspended in chloroform, is treated with slightly more than the theoretical quantity (2 mols.) of chlorine, *dichlorodithymol*, $C_{20}H_{24}O_2Cl_2$, is formed as brilliant, slightly yellow, prismatic crystals, m. p. 152—153° (corr.). By the continued action of chlorine, or, better, by the action of bromine (1 mol.) on its chloroform solution, dichlorodithymol is oxidised to *dichlorodithymoquinone*, $C_{20}H_{22}O_2Cl_2$, which forms radiating groups of deep garnet-red, prismatic needles, m. p. 130—132° (corr. decomp.), insoluble in alkalis, and giving an intense blue colour with tincture of guaiacum.

Dithymol, suspended in chloroform, is converted by the prolonged action of chlorine into *dichlorodithymoquinone dichloride*,

$C_{20}H_{22}O_2Cl_4$,

a substance forming small, prismatic crystals of a sulphur-yellow colour, m. p. 176—178° (corr. decomp.), insoluble in alkalis. The latter substance on reduction gives dichlorodithymol. E. H.

Styrene Oxide. MARC TIFFENEAU and ERNEST FOURNEAU (*Compt. rend.*, 1908, **146**, 697—699).—Styrene oxide, obtained in a yield of 50% by the action of powdered potassium hydroxide on an ethereal solution of styrene iodohydrin (Abstr., 1905, i, 591; this vol., i, 19), has b. p. 191—192° (corr.) or 84—85°/15 mm., D^0 1·0633, $D^{16·4}$ 1·0523; it is not appreciably changed when heated in a sealed tube above its boiling point, and is only slowly converted into the isomeric phenylacetaldehyde on boiling with dilute mineral acids (Abstr., 1907, i, 404). Styrene oxide is reduced by sodium and water to benzyl alcohol, and combines with halogen acids to form halohydrins (Abstr., 1907, i, 404); when heated in a sealed tube with hydrocyanic acid, it yields the cyanohydrin of phenylacetaldehyde, which is converted into a mixture of ethyl phenylhydracrylate and ethyl cinnamate by the action of an alcoholic solution of hydrogen chloride. Styrene oxide condenses with organo-magnesium derivatives to form the corresponding substituted benzylcarbinol, $CH_2Ph·CHR·OH$, and not the alcohol, $CH_2R·CHPh·OH$, as previously stated (Abstr., 1907, i, 818), and is converted quantitatively into the corresponding amino-alcohol when heated in a sealed tube with amines (compare Krassusky, this vol., i, 139). M. A. W.

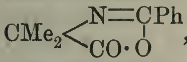
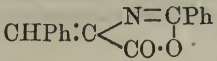
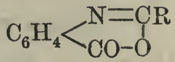
Oxidation of *m*-Nitrobenzoylcarbinol. William L. Evans and Benjamin T. Brooks (*J. Amer. Chem. Soc.*, 1908, 30, 404—412).—In an earlier paper (Evans, Abstr., 1906, i, 269), an account has been given of the behaviour of benzoylcarbinol towards oxidising agents. Further work is being carried out with the object of ascertaining whether the substituted benzoylcarbinols follow the same general course of reaction, and of determining the effect of substitution on the behaviour of these substances. The present paper deals with the oxidation of *m*-nitrobenzoylcarbinol.

An improved method is described for the preparation of bromo-*m*-nitroacetophenone. m-*Nitroacetophenone acetate* has m. p. 51°. On hydrolysis, it yields m-*nitrobenzoylcarbinol*, m. p. 92·5—93°, which forms pale yellow crystals, and, when heated with a mixture of glacial acetic acid and acetyl chloride, is reconverted into *m*-nitroacetophenone acetate. Aqueous solutions of the carbinol reduce ammoniacal silver nitrate and Fehling's solution.

When the carbinol is treated with freshly-precipitated mercuric oxide, freshly-precipitated silver oxide, or potassium permanganate, either alone or in presence of alkali hydroxide, it yields only *m*-nitrobenzoic acid and carbon dioxide. By the action of cupric hydroxide and alkali hydroxide on the carbinol, it is converted into *m*-nitromandelic acid, whilst, if treated with potassium ferricyanide and potassium hydroxide, it yields both *m*-nitrobenzoic and *m*-nitromandelic acids. E. G.

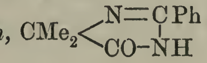
Preparation of Eugenyl *o*- and *m*-Aminobenzoates. J. D. Riedel (D.R.-P. 189333).—*Eugenyl* o-*nitrobenzoate*, pale yellow prisms, m. p. 60—62°, and *eugenyl* m-*nitrobenzoate*, well-defined, yellow prisms, m. p. 71—72°, are obtained by the action of the respective nitrobenzoyl chlorides on eugenol in the presence of aqueous sodium hydroxide. The corresponding amino-esters are produced on reducing the foregoing nitro-compounds with tin and hydrochloric acid or zinc and acetic acid; *eugenyl* o-*aminobenzoate*, yellowish-white, lustrous plates, m. p. 98—99°; *acetyl* derivative, yellowish-white needles, m. p.

102—103°; *eugenyl* m-*aminobenzoate*, yellow, lustrous prisms, m. p. 72—73°; *hydrochloride*, yellowish-white flakes, m. p. 160—162°; *acetyl* derivative, colourless plates, m. p. 102°. G. T. M.

Benzoylamino*iso*butyrolactimone. Ernst Mohr and Theodor Geis (*Ber.*, 1908, **41**, 798—799).—Mohr and Köhler obtained an anhydride, termed a lactimone, by heating *o*-aminobenzoylanthranilic acid with acetic anhydride (Abstr., 1907, i, 414). A similar anhydride,  $\mathrm{CMe_2}<\begin{array}{l}\mathrm{N{=}CPh}\\ \mathrm{CO\cdot O}\end{array}$, which contains the typical lactime and lactone groupings, $\cdot\mathrm{O\cdot C{:}N}\cdot$ and $\cdot\mathrm{C\cdot CO\cdot O\cdot C}\cdot$, and is therefore a lactimone, has now been obtained in the same manner from α-benzoylamino*iso*butyric acid. The lactimone group includes also such substances as the yellow lactimide of benzylidenehippuric acid,  $\mathrm{CHPh{:}C}<\begin{array}{l}\mathrm{N{=}CPh}\\ \mathrm{CO\cdot O}\end{array}$ (Erlenmeyer, jun., Abstr., 1899, i, 759), and the acylanthranils,  $\mathrm{C_6H_4}<\begin{array}{l}\mathrm{N{=}CR}\\ \mathrm{CO{-}O}\end{array}$ (Anschütz, Schmidt, and Greiffenberg, Abstr., 1903, i, 57).

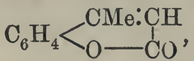
α-*Benzoylamino*iso*butyric acid*, $\mathrm{NHBz\cdot CMe_2\cdot CO_2H}$, prepared in a 60—65% yield by the action of benzoyl chloride and potassium hydrogen carbonate on α-amino*iso*butyric acid in cold concentrated aqueous solution, crystallises in colourless plates, m. p. 198°, decomp. above 220°. The *lactimone*, $\mathrm{C_{11}H_{11}O_2N}$, crystallises in colourless plates, m. p. 34°, b. p. 123°/9 mm., and when treated with cold saturated alcoholic ammonia forms α-*benzoylamino*iso*butyramide*,

$$\mathrm{NHBz\cdot CMe_2\cdot CO\cdot NH_2},$$

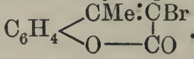
which crystallises in white needles, m. p. 201°. When boiled with aqueous sodium hydroxide, the amide evolves small amounts of ammonia and yields the *lactam*,  $\mathrm{CMe_2}<\begin{array}{l}\mathrm{N{=}CPh}\\ \mathrm{CO{-}NH}\end{array}$ (?), crystallising in in white needles, m. p. 202°. G. Y.

Preparation of the Urethane of *m*-Amino-*p*-ethoxybenzoic Acid. Aktiengesellschaft für Anilin-Fabrikation (D.R.-P. 189838).—The *urethane*, $\mathrm{CO_2Et\cdot NH\cdot C_6H_3(OEt)\cdot CO_2H}$, of 3-amino-4-ethoxybenzoic acid is produced by dissolving the hydrochloride of this amino-acid in aqueous sodium carbonate and adding ethyl chlorocarbonate; it crystallises from alcohol in needles, m. p. 211—212°, and has a very soluble sodium salt. G. T. M.

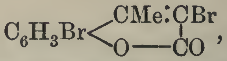
4-Methylcoumarin. F. Peters and Hugo Simonis (*Ber.*, 1908, **41**, 830—837).—The synthesis of methylcoumarin from ethyl acetoacetate and phenol by von Pechmann's method (Abstr., 1884, **66**, 1331) gives poor yields, owing probably to the concentrated sulphuric acid used acting rather to sulphonate the phenol than to cause condensation. Using a less concentrated acid (73% $\mathrm{H_2SO_4}$) which no longer acts as a sulphonating agent and less phenol, and stirring the mixture rapidly, a more satisfactory yield is obtained. The proof of the constitution of 4-methylcoumarin is given by conversion into methylcoumarilic acid (Hantzsch and Lang, Abstr., 1886, 706). A number of halogen derivatives are now described. 4-Methylcoumarin,

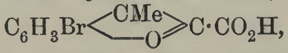


$$C_6H_4{<}\genfrac{}{}{0pt}{}{CMe:CH}{O\text{---}CO},$$

forms long, colourless needles, m. p. 90°; the *dibromide* is unstable, and forms minute, red needles which lose hydrogen bromide on drying, giving 3-*bromo*-4-*methylcoumarin*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CMe:CBr}{O\text{---}CO}$. This crystallises in colourless prisms, m. p. 114°; when heated with concentrated potassium hydroxide, it forms the *potassium* salt of 2-methylcoumarilic acid, crystallising in silky, glistening needles; the acid forms feather-like prisms, m. p. 188° (compare Hantzsch, *loc. cit.*); the copper salt forms green needles containing $3H_2O$, and the methyl ester, long, glistening needles, m. p. 70°.

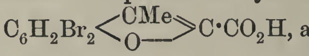
4-*Methyldihydrocoumarin* crystallises in colourless, monoclinic prisms, m. p. 278°.

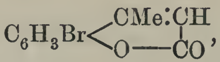
3 : 6-*Dibromo*-4-*methylcoumarin*,  $C_6H_3Br{<}\genfrac{}{}{0pt}{}{CMe:CBr}{O\text{---}CO}$, prepared by the action of bromine in carbon disulphide solution in sealed tubes at 140°, crystallises in yellow needles, m. p. 167°. Alkali converts it into 4-*bromo*-2-*methylcoumarilic acid*,

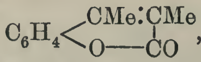


$$C_6H_3Br{<}\genfrac{}{}{0pt}{}{CMe}{O}{>}C\cdot CO_2H,$$

separating from benzene in aggregates of yellow needles, m. p. 155°, and forming a *copper* salt ($+2H_2O$), bright green needles, and a *potassium* salt ($+2H_2O$), silky, glistening needles.

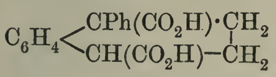
3 : 6 : 8-*Tribromo*-4-*methylcoumarin*, prepared by heating with bromine under pressure at 175°, separates in colourless prisms, m. p. 196°. It yields, when heated with potassium hydroxide, 4 : 6-*dibromo*-2-*methylcoumarilic acid*,  $C_6H_2Br_2{<}\genfrac{}{}{0pt}{}{CMe}{O}{>}C\cdot CO_2H$, a yellow, flocculent precipitate, m. p. 96°; the *copper* salt ($+2H_2O$) forms green, microscopic needles.

6-*Bromo*-4-*methylcoumarin*,  $C_6H_3Br{<}\genfrac{}{}{0pt}{}{CMe:CH}{O\text{---}CO}$, prepared from *p*-bromophenol and ethyl acetoacetate, forms colourless needles, m. p. 187°. It yields a mixture of 3 : 6- and 6 : 8-dibromomethylcoumarins when brominated, and the 3 : 6 : 8-tribromomethylcoumarin on further bromination. This last compound, when oxidised with permanganate in alkaline solution, gives 3 : 5-dibromosalicylic acid, thereby fixing the position of the bromine atom 3.

3 : 4-*Dimethylcoumarin*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CMe:CMe}{O\text{---}CO}$, prepared by condensing ethyl methyl acetoacetate with phenol, has m. p. 115°, and is isomeric with von Pechmann's 4 : 6-dimethylcoumarin (Abstr., 1885, 56).

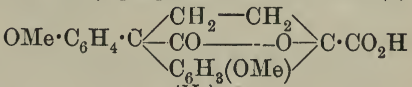
E. F. A.

Comparative Study of the Dehydration of Atrolactic and *p*-Methoxyatrolactic Acids. *p*-Methoxyatropic and Di-*p*-methoxyatropic Acids. J. BOUGAULT (*Compt. rend.*, 1908, 146, 766—769. Compare Abstr., 1902, i, 452).—*p*-Methoxyatrolactic acid is markedly different from atrolactic acid in its relation to dehydrating agents. Ladenburg found (Abstr., 1883, 670) that atrolactic acid is dehydrated by prolonged boiling with dilute hydrochloric acid, giving atropic acid and a little of Fittig's *iso*atropic acid; the author obtains the same transformation by heating for thirty minutes with concentrated hydrochloric acid on a boiling water-bath. By the very prolonged action (five to six months) of cold hydrochloric acid, however, β-chlorohydratropic acid, $CH_2Cl\cdot CHPh\cdot CO_2H$, is the chief product, together with a small quantity of *iso*atropic acid. Atrolactic acid does not give appreciable quantities of atropic acid when boiled with acetic or very dilute mineral acids. On the other hand, *p*-methoxyatrolactic acid is rapidly dehydrated by boiling with these acids, giving good yields of p-*methoxyatropic acid*, $OMe\cdot C_6H_4\cdot C(CO_2H){:}CH_2$, shining spangles, m. p. 119—120°, which forms a *dibromide*, m. p. 142°. When *p*-methoxyatrolactic acid is left in contact with cold concentrated hydrochloric acid for forty-eight hours, the product is a mixture in almost equal parts of *p*-methoxyatropic acid and a dimolecular condensation derivative of this, called by the author *bis*-p-*methoxyatropic acid*, $(C_{10}H_{10}O_3)_2$. At the temperature of the water-bath, the latter acid is the sole product, and the reaction is complete in fifteen to twenty minutes. Bis-*p*-methoxyatropic acid has m. p. 215°, and by titration with standard alkali its molecular weight is found to be 356 (calculated as a monobasic acid). Re-titration after boiling with slight excess of alkali gives the result 178 (also calculated as a monobasic acid), indicating that the substance is a lactonic acid. Fittig (Abstr., 1881, 425) proposed the formula (I)



$$C_6H_4<\begin{matrix}CPh(CO_2H)\cdot CH_2\\ |\\ CH(CO_2H)-CH_2\end{matrix}$$

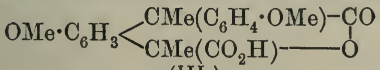
(I.)



$$OMe\cdot C_6H_4\cdot C\begin{matrix}\diagup CH_2-CH_2\diagdown\\ -CO\text{———}O\!-\\ \diagdown C_6H_3(OMe)\diagup\end{matrix}C\cdot CO_2H$$

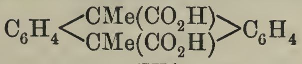
(II.)

for *iso*atropic acid, from which the formula (II) would be deduced for bis-*p*-methoxyatropic acid. The author, however, considers that a direct combination of the $\cdot CH_2\cdot$ groups is improbable, and prefers the formula (III) for the new acid, and accordingly represents Fittig's



$$OMe\cdot C_6H_3<\begin{matrix}CMe(C_6H_4\cdot OMe)-CO\\ |\\ CMe(CO_2H)\text{———}O\end{matrix}$$

(III.)



$$C_6H_4<\begin{matrix}CMe(CO_2H)\\ CMe(CO_2H)\end{matrix}>C_6H_4$$

(IV.)

*iso*atropic acid by (IV), which explains more easily than (I) its oxidation to anthraquinone. E. H.

Tyrosine. Jules Aloy and Charles Rabaut (*Bull. Soc. chim.*, 1908, [iv], 3, 391—393).—A study of the action of various reagents on tyrosine. The *hydrobromide* and *hydriodide* of the base, which are both crystalline, are described. Bromine vapour converts the base into dibromotyrosine hydrobromide, but with excess of bromine water an unstable, yellow perbromide is obtained, which is soluble in alkalis and most organic solvents. Dry chlorine has no action on the base, but in presence of moisture a yellow, unstable, perchlorinated product is formed, which blackens on exposure to air. No definite derivatives can be obtained by the action of iodine vapour on tyrosine.

Tyrosine suspended in water or dissolved in hydrochloric acid gives, on addition of chlorine water, followed by ammonia solution, a fine red colour. Bromine water may be used in place of chlorine water, but the colour formed is then less intense. Leucine does not give this reaction. T. A. H.

Catalytic Reactions at High Temperatures and Pressures. XVI. Reduction of Aromatic Ethers, Esters, and Acids in Presence of Nickel Oxide. Wladimir N. Ipatieff and O. Philipoff (*Ber.*, 1908, **41**, 1001—1007).—Phenyl ether is reduced by hydrogen in presence of nickel oxide at 230°/100 atmospheres in twelve hours, forming *cyclo*hexane, *cyclo*hexanol, and cyclo*hexyl ether*, $O(C_6H_{11})_2$, which is formed also, together with *cyclo*hexanol, by reduction of phenol in the same manner, and is obtained as a viscid oil, b. p. 275—277°/760 mm. Ethyl phthalate, when heated with hydrogen and nickel oxide under high pressures, yields methane, carbon dioxide, *o*-toluic acid, phthalic acid, and small amounts of benzoic acid.

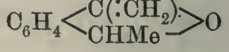
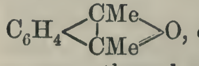
Potassium phthalate remains unchanged when mixed with nickel oxide and heated in a current of hydrogen at 300°, or if heated with hydrogen alone under pressure, but, if heated with hydrogen and nickel oxide under pressure at 300°, it is reduced to *trans-cyclo*hexane-1 : 2-dicarboxylic acid, together with small amounts of benzoic acid and methane; the amount of these by-products increases rapidly with the temperature of the reaction. This reduction is recommended as the most convenient method of preparing the *trans-cyclo*hexanedicarboxylic acid.

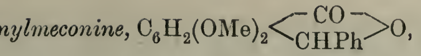
Under the same conditions, potassium benzoate is reduced in nine hours to the extent of 40—50%, yielding potassium *cyclo*hexanecarboxylate; at temperatures above 320°, the yield decreases in consequence of increased formation of methane. The *cyclo*hexanecarboxylic acid is best prepared by heating sodium benzoate, which is more easily reduced than the potassium salt, with hydrogen and nickel oxide under pressure at 300° for two periods of four hours each.

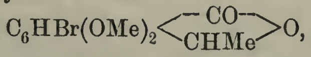
G. Y.

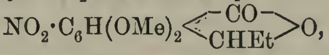
Phthalides and Meconines. Eric Mermod and Hugo Simonis (*Ber.*, 1908, **41**, 982—985).—The condensation of organo-magnesium compounds with phthalaldehydic acid and opianic acid has been continued (compare Abstr., 1906, i, 32, 303).

α-Ethylphthalide (compare Gottlieb, Abstr., 1899, i, 512) and α-phenylphthalide (Graebe and Juillard, Abstr., 1888, 1095) have been prepared from phthalaldehydic acid.

Anhydro-αα′-dimethylhydrophthalide,  $C_6H_4<\begin{matrix}C(:CH_2)\\CHMe\end{matrix}>O$ or  $C_6H_4<\begin{matrix}CMe\\|\\CMe\end{matrix}>O$, obtained by the action of magnesium methyl iodide on an ethereal solution of α-methylphthalide (Abstr., 1906, i, 32), crystallises from dilute alcohol in colourless needles, m. p. 153° (decomp.) after sintering at 140°.

α-Phenylmeconine,  $C_6H_2(OMe)_2{<}\substack{-CO-\\ CHPh}{>}O$, crystallises from alcohol in glistening prisms, m. p. 112°. When warmed with alkalis, the ring is ruptured, but closes again on the addition of acid. The meconine dissolves in cold concentrated sulphuric acid to a colourless solution, which assumes a purple colour when warmed.

Magnesium alkyl or aryl bromides do not react with phthalaldehydic or opianic acid. Bromoalkylmeconines can be obtained either by the condensation of Grignard's compound with bromo-opianic acid or by the bromination of the alkylmeconines. *Bromo-α-methylmeconine*,  $C_6HBr(OMe)_2{<}\substack{-CO-\\ CHMe}{>}O$, forms colourless plates, m. p. 77°, and the corresponding *ethyl* compound has m. p. 79°.

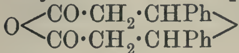
Nitro-α-ethylmeconine,  $NO_2{\cdot}C_6H(OMe)_2{<}\substack{-CO-\\ CHEt}{>}O$, obtained by the action of fuming nitric acid on ethylmeconine, crystallises from alcohol in yellow plates, m. p. 103·5°. When reduced, it yields *amino-α-ethylmeconine*, $C_{12}H_{15}O_4N$, in the form of colourless prisms, m. p. 158°. The *hydrochloride*, $C_{12}H_{15}O_4N,HCl$, forms sparingly soluble, glistening needles, m. p. 196° (decomp.). The *platinichloride* forms a brown precipitate, which decomposes at 172°, and the *aurichloride* a dark green precipitate, decomposing at 200°. J. J. S.

Synthesis of Certain Aromatic Succinic Acids. Samuel Avery and Fred W. Upson (*J. Amer. Chem. Soc.*, 1908, **30**, 600—604).—In order to compare the αβ-diphenylglutaric acid obtained by Avery and McDole (compare following abstract) with its isomeride, *α-phenyl-β-benzylsuccinic acid*, $CO_2H{\cdot}CHPh{\cdot}CH(CH_2Ph){\cdot}CO_2H$, the latter was prepared by the condensation of ethyl sodiobenzylmalonate with ethyl bromophenylacetate; it crystallises in slender, white needles, m. p. 176°; the *silver* salt is a white, amorphous precipitate. The investigation was then extended to see if sodium benzyl cyanide could be made to condense with aldehyde cyanohydrins in the same way as ethyl sodiocyanoacetate, as described by Higson and Thorpe (Trans., 1906, **89**, 1455). This was found to be the case; thus the nitrile of αβ-diphenylsuccinic acid (compare Chalaney and Knoevenagel, Abstr., 1892, 619) was obtained from sodium benzyl cyanide and benzaldehyde cyanohydrin. In some cases, one of the cyano-groups undergoes saponification during the reaction. This seems to depend on the nature of the adjacent groups; for example, *β-cyano-β-phenyl-α-*iso*propylpropionic acid*, $CN{\cdot}CHPh{\cdot}CHPr^{\beta}{\cdot}CO_2H$, is formed by condensing sodium benzyl cyanide with *iso*butaldehyde cyanohydrin; it forms white, feathery crystals, m. p. 126°, and when heated with strong hydrochloric acid under pressure is converted into *β-phenyl-α-*iso*propylsuccinic acid*, $CO_2H{\cdot}CHPr^{\beta}{\cdot}CHPh{\cdot}CO_2H$, crystallising in colourless, microscopic plates, m. p. 178°. W. H. G.

Action of Sodium Benzyl Cyanide with Cinnamic Ester. Samuel Avery and Guy R. McDole (*J. Amer. Chem. Soc.*, 1908, **30**, 595—600).—The action of benzyl cyanide on ethyl cinnamate was studied with the object of preparing certain aryl glutaric acids. It was thought probable that the reaction would take place in a manner similar to that observed by Michael (Abstr., 1887, 672) in the action of ethyl sodioacetoacetate on the esters of unsaturated acids, namely, in the formation of a compound having the constitution

$$CN{\cdot}CHPh{\cdot}CHPh{\cdot}CHNa{\cdot}CO_2R.$$

It was found, however, that the ester had undergone saponification, the two principal products formed being sodium γ-cyano-βγ-diphenylbutyrate and a compound to which is provisionally given the formula



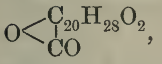
$O<\begin{matrix}CO{\cdot}CH_2{\cdot}CHPh\\CO{\cdot}CH_2{\cdot}CHPh\end{matrix}>CPh{\cdot}CN$; this formula is in harmony with the observed facts, except in the following: the compound appears to be unchanged when boiled with sodium carbonate or ammonia in aqueous or alcoholic solution, and, although it is converted into a salt when boiled with alcoholic potassium hydroxide, the acid liberated from the salt has resisted all attempts to reconvert it into an anhydride. *γ-Cyano-βγ-diphenylbutyric acid*, $CN{\cdot}CHPh{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, prepared by the interaction of benzyl cyanide and ethyl cinnamate in the presence of solid sodium methoxide, crystallises in glistening, white needles, m. p. 161·5°. When heated with strong hydrochloric acid in a sealed tube at 150° for three hours, it is converted into *αβ-diphenylglutaric acid*, $CO_2H{\cdot}CHPh{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, crystallising in needles, m. p. 223—224°; the *silver* salt, $C_{17}H_{14}O_4Ag_2$, was prepared. The anhydride could not be obtained; the *anilide*, $C_{23}H_{21}O_3N$, crystallises in flat needles with a pearly lustre, m. p. 230—232°. The *substance*, $CN{\cdot}CPh(CHPh{\cdot}CH_2{\cdot}CO)_2O$ (?), is obtained when a mixture of benzyl cyanide and dry sodium methoxide heated to 140° is added to hot ethyl cinnamate, the whole being kept at 140° for ten minutes. It crystallises in long, obliquely pointed plates, m. p. 231—232°; when heated with a strong alcoholic potassium hydroxide solution, it is converted into the *potassium* salt of an acid; the free *acid*, $C_{26}H_{23}O_4N$, crystallises in rectangular plates, m. p. 213°; the *silver* salt is a white, insoluble powder. W. H. G.

Marrubiin. Henry M. Gordin (*J. Amer. Chem. Soc.*, 1908, **30**, 265—271).—Marrubiin, the bitter constituent of horehound (*Marrubium vulgare*), was first investigated by Harms, and later by Kromayer, Hertel, Morrison, and Matusow.

Marrubiin, $C_{21}H_{28}O_4$, has m. p. 154·5—155·5°, b. p. 297—299°/15 mm., $[\alpha]_D$ +45·68°, and when crystallised slowly from alcohol forms large, monoclinic prisms [$a:b:c = 1{\cdot}5551:1:0{\cdot}885$; $\beta = 61°17'$], but, when crystallised rapidly, forms flat, tabular prisms, which also belong to the monoclinic system. The compound does not contain any methoxyl groups, and does not decolorise bromine solution. It has a bitter taste, a neutral reaction, and does not contain hydroxyl or carbonyl groups. When boiled with alcoholic potassium hydroxide, it is converted into *potassium marrubate*.

Marrubic acid, $C_{20}H_{29}O_3{\cdot}CO_2H$, m. p. 173—174° and $[\alpha]_D$ +7·86°, forms long, white, silky needles, and when heated at 190—200° under 15 mm. pressure is reconverted into marrubiin. The same change can be brought about by heating the acid at 50° with acetic anhydride containing a trace of zinc chloride, or by boiling it with alcoholic hydrochloric acid. The acid reduces ammoniacal silver nitrate and Fehling's solution. The *barium* salt is described. The *ethyl* ester, m. p. 87°, forms lustrous scales, and, when heated at 100° under 28 mm. pressure, is converted into marrubiin.

The results of the investigation indicate that marrubiin is a lactone,



$O<\begin{matrix} C_{20}H_{28}O_2 \\ | \\ CO \end{matrix}>$, behaving like a γ-lactone in taking up a molecule of water to form a hydroxy-acid, marrubic acid, $OH\cdot C_{20}H_{28}O_2\cdot CO_2H$.

E. G.

Synthesis of Optically Active Dibenzylaspartic and Dibenzylmalamic Acids. OSCAR LUTZ (*Ber.*, 1908, 41, 841—847).—Fischer and Raske (Abstr., 1907, i, 381) have shown that under certain conditions *d*-aspartic acid is formed from *l*-bromosuccinic acid; the chief product, however, is malamic acid. It appears on further study of this reaction that, in addition to the influence of temperature, the strength and constitution of the base employed have also to be taken into account. By the action of dibenzylamine, a weaker base, on *l*-chloro- or -bromo-succinic acid, d-*dibenzylaspartic acid* is formed to the extent of 65—70%, and l-*dibenzylmalamic acid* to the extent of 8—15%. The former, $N(C_7H_7)_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, forms thread-like, matted needles, m. p. 152—153°, is relatively stable towards heat and barium hydroxide, and forms a *silver* salt, $C_{18}H_{17}O_4NAg_2$. In ethyl alcohol, $[\alpha]_D = 0°$; in sodium hydroxide solution, $[\alpha]_D = +23\cdot2°$; in presence of benzylamine, it has $[\alpha]_D$ + 43·8° in ethyl alcohol, +4° in methyl alcohol, −10° in acetone, and −5·2° in acetic acid.

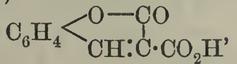
l-*Dibenzylmalamic acid*, $CO_2H\cdot CH(OH)\cdot CH_2\cdot CO\cdot N(C_7H_7)_2$, forms minute prisms, m. p. 169—170° (decomp.); it loses water when heated, and forms an optically inactive unsaturated compound. It has $[\alpha]_D$ −61·6° in ethyl alcohol or −26·4° in presence of benzylamine.

E. F. A.

Action of Ozone on Santonin. GUIDO BARGELLINI and CESARE GIALDINO (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 248—249).—The action of ozone on a chloroform solution of santonin or on a faintly alkaline solution of sodium santoninate yields an acid apparently identical with the ketonic acid, $C_{15}H_{20}O_7$, obtained by Angeli and Marino (Abstr., 1907, i, 321) by the oxidation of santonic acid with potassium permanganate.

T. H. P.

Preparation of Coumarincarboxylic Acid. HAARMANN and REIMER (D.R.-P. 189252).—*Coumarin-3-carboxylic acid*,



$$C_6H_4<\begin{matrix} O-CO \\ \quad\ \ | \\ CH:C\cdot CO_2H \end{matrix},$$

m. p. 187—188°, was obtained by condensing cyanoacetic acid and salicylaldehyde in alkaline solution to *o*-hydroxybenzylidenecyanoacetic acid, and hydrolysing this intermediate product with steam and concentrated hydrochloric acid.

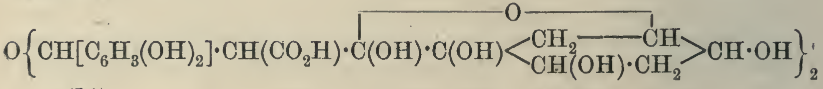
G. T. M.

Coffee. II. K. GORTER (*Annalen*, 1908, 359, 217—244. Compare this vol., i, 186).—In continuation of his investigation of the constituents of coffee extract, the author has studied the decomposition products of chlorogenic acid, and describes some further new substances obtained from the coffee beans.

When treated with aqueous potassium hydroxide at the ordinary temperature, chlorogenic acid yields caffeic and quinic acids, but, if boiled with dilute mineral acids, decomposes to the extent of 70%, forming carbon dioxide and a *product*, which is reddish-violet with blue fluorescence in solution, and to the extent of 30% is hydrolysed to caffeic and quinic acids. The colour reactions of these two acids, and the *zinc*, $(C_7H_{11}O_6)_2Zn$, and *calcium*, $(C_7H_{11}O_6)_2Ca,10H_2O$, salts of quinic acid, are described.

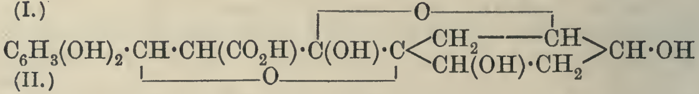
The action of acetic anhydride, containing small amounts of sulphuric acid, on chlorogenic acid at the ordinary temperature leads to the formation of *penta-acetylhemichlorogenic acid*, $C_{16}H_{13}O_9Ac_5$, which crystallises from dilute alcohol in white needles, m. p. 180·5—181°, and has a bitter taste; the *aniline* salt, $C_{16}H_{13}O_9Ac_5,NH_2Ph$, white crystals, m. p. 142—143°. On hydrolysis with acids or alkalis, the penta-acetyl compound yields *hemichlorogenic acid*; this is isolated as the *aniline* salt, $C_{16}H_{18}O_9,NH_2Ph$, crystallising in white needles, m. p. 173°. A mixture of this salt with the *aniline* salt of chlorogenic acid, $C_{32}H_{38}O_{19},2NH_2Ph$, m. p. 174°, has m. p. 165—166°. The *benzidine* salt, needles, m. p. 161°, is more readily soluble than the corresponding chlorogenate.

The consideration of these facts leads to the formulation of the annexed constitutions for chlorogenic acid (I) and hemichlorogenic acid (II):



$$\mathrm{O}\left\{\mathrm{CH[C_6H_3(OH)_2]\cdot CH(CO_2H)\cdot \overbrace{C(OH)\cdot C(OH)<{CH_2\text{——}CH \atop CH(OH)\cdot CH_2}}^{O}>CH\cdot OH}\right\}_2$$

(I.)



$$\mathrm{C_6H_3(OH)_2\cdot \underbrace{CH\cdot CH(CO_2H)\cdot \overbrace{C(OH)\cdot C<{CH_2\text{——}CH \atop CH(OH)\cdot CH_2}}^{O}}_{O}>CH\cdot OH}$$

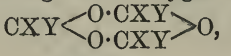
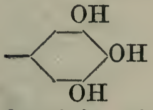
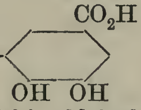
(II.)

Addition of alcohol to the first extract of Liberian or Arabian coffee beans precipitates a *pectin substance*, $[\alpha]_D$ +15°, which has a feeble acid reaction, dissolves slowly in water, when heated with dilute mineral acids yields galactose and a pentose, and on oxidation with nitric acid forms mucic acid.

Coffalic acid, $C_{34}H_{54}O_{15}$, is obtained on evaporation of the mother liquor from the preparation of potassium-caffeine chlorogenate; it crystallises in colourless, rhombic prisms, m. p. 255°, has a sweet taste, forms *precipitates* with silver nitrate, copper sulphate, and lead acetate and ammonia, and on hydrolysis with alkalis or acids yields *iso*valeric acid and an amorphous *substance*, which commences to soften at 160°, m. p. about 255°.

Liberian coffee beans contain an *oxydase*, which gives yellow, changing to yellowish-green and reddish-brown, coloration with potassium caffeine chlorogenate, and is therefore the cause of the colour gradually acquired by the colourless beans after plucking; the oxydase is destroyed at 70°, and gives a coloration with guaiacol solutions resembling, but less intense than, that given by laccase.

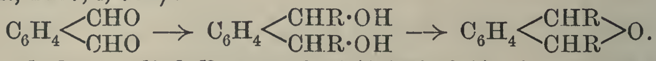
The caffetannic acid, described by previous authors, is a mixture of chlorogenic and coffalic acids with other substances. G. Y.

Preliminary Note on the Constitution of Gallotannic Acid and of Tannins in General. Stewart J. Lloyd (*Chem. News*, 1908, 97, 133).—From molecular weight determinations of crystalline compounds of gallotannic acid, notably the penta-acetyl derivative, it is concluded that natural gallotannic acid is composed of three digallic acid groups united to each other through three oxygen atoms to form a six-membered ring of the type  $\mathrm{CXY}{<}\substack{\mathrm{O{\cdot}CXY}\\ \mathrm{O{\cdot}CXY}}{>}\mathrm{O}$, in which X =  and Y = O—, analogous to that found in trithio-ketones and trithio-aldehydes. Such a configuration admits of an inactive *cis*-form as well as the active *trans*-form which is assigned to natural gallotannic acid. P. H.

Catalytic Reactions at High Temperatures and Pressures. XIV. Reduction of Benzaldehyde and Benzyl Alcohol in Presence of Iron. Wladimir N. Ipatieff (*Ber.*, 1908, 41, 993—995. Compare Abstr., 1907, i, 5, 827).—It was shown previously that aliphatic aldehydes and ketones are reduced to the corresponding alcohols by hydrogen in presence of iron at high temperatures and pressures, and that, on the other hand, aromatic alcohols, aldehydes, and ketones under similar conditions, but in presence of nickel oxide, yield *cyclo*polymethylenes. It is now found that when heated with hydrogen in an iron tube for twelve hours at 280°/100 atmospheres, benzaldehyde yields water, toluene, dibenzyl, and resins. It is considered that the reduction must lead in the first place to the formation of benzyl alcohol; part of this is reduced directly to toluene, whilst another part forms water and benzyl ether, which on further reduction yields toluene and dibenzyl. In agreement with this view, it is found that benzyl alcohol under similar conditions yields toluene, benzaldehyde, and dibenzyl. Moreover, whilst reduction of the alcohol in a copper tube leads to the formation of toluene and small amounts of dibenzyl, benzaldehyde, which as previously shown does not form benzyl alcohol when heated with hydrogen in presence of copper, under these conditions also does not yield dibenzyl. In the absence of hydrogen, benzyl alcohol decomposes when heated in an iron tube at 400°, forming hydrogen and benzaldehyde, which partly decomposes further to benzene and carbon monoxide and partly is reduced by the hydrogen, forming toluene and dibenzyl. G. Y.

Reaction between Potassium Cyanide and *o*-Nitrobenzaldehyde. S. Ekecrantz and A. Ahlqvist (*Ber.*, 1908, 41, 878—881).—The authors have examined the action of potassium cyanide on *o*-nitrobenzaldehyde under Popovici's conditions (Abstr., 1907, i, 628), and conclude that her so-called 2 : 2′-dinitrobenzoin consists of *o*-nitrosobenzoic acid and *o*-azoxybenzoic acid, and that her 2 : 2′-dinitrobenzil is *o*-nitrobenzoic acid. C. S.

Action of Grignard Compounds on *o*-Phthalaldehyde. F. Nelken and Hugo Simonis (*Ber.*, 1908, **41**, 986—989).—*o*-Phthalaldehyde condenses with an excess of magnesium alkyl iodides, yielding *o*-dihydroxyalkylbenzenes, which when distilled form alkyl derivatives of *iso*coumaran or 1 : 3-dialkylphthalans (compare Ludwig, Abstr., 1907, i, 702):



$$C_6H_4{<}\begin{matrix}CHO\\CHO\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CHR{\cdot}OH\\CHR{\cdot}OH\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CHR\\CHR\end{matrix}{>}O.$$

Di-a-hydroxy-o-diethylbenzene, $C_6H_4(CHMe{\cdot}OH)_2$, is a yellow, viscid oil, which solidifies when placed in a freezing mixture. It dissolves readily in practically all solvents, and when distilled under reduced pressure yields 1 : 3-*dimethylphthalan* as a pale yellow oil, b. p. 122°/50 m.m.

Di-a-hydroxy-o-dipropylbenzene, $C_6H_4(CHEt{\cdot}OH)_2$, is an oil, and the corresponding 1 : 3-*diethylphthalan* has b. p. 137°/50 mm.

1 : 3-*Diphenylphthalan* has b. p. 240°/14 mm., and forms a limpid, yellowish-red oil. J. J, S.

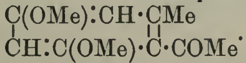
[Preparation of Vanillin from Guaiacol.] A. Roesler (D.R.-P. 189037).—The formation of an aldimide compound does not occur with guaiacol, hydrogen cyanide, and hydrochloric acid except when the reagents are brought together in the capillary interstices of infusorial earth. This earth is mixed with aqueous zinc chloride and heated to dryness, then treated with a benzene solution of guaiacol and hydrogen cyanide, and saturated with hydrogen chloride. The intermediate aldimide hydrochloride, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}NH,HCl$, is decomposed with water, and the vanillin extracted with ether and purified by means of its bisulphite compound. G. T. M.

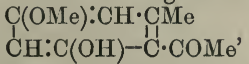
Synthesis of Trimethylgallaldehyde. Ferdinand Mauthner (*Ber.*, 1908, **41**, 920—925).—The close relationships existing between gallaldehydes and some natural products suggested the above synthesis. Trimethylgallyl chloride (Perkin and Weizmann, Trans., 1906, **89**, 1655) was first condensed with hydrogen cyanide in ethereal solution in the presence of pyridine to form 3 : 4 : 5-*trimethoxybenzoyl cyanide*, $C_{11}H_{11}O_4N$, which crystallises in yellow needles from light petroleum; m. p. 136—137°. It is hydrolysed on warming with dilute acids or alkalis to trimethylgallic acid, but the cyanide and hydrochloric acid (D 1·19) at the ordinary temperature after ten days yield a mixture of (1) *trimethoxyphenylglyoxylamide*, $C_6H_2(OMe)_3{\cdot}CO{\cdot}CO{\cdot}NH_2$, in small amount, crystallising from benzene in colourless needles, m. p. 149—150°, which on heating with acids or alkalis give trimethylgallic acid, ammonia and carbon monoxide, and (2) a good yield of *trimethoxyphenylglyoxylic acid*, $C_{11}H_{12}O_6$, separating from benzene in colourless needles, m. p. 155—156°; the *phenylhydrazone*, $C_{17}H_{18}O_5N_2$, forms yellow needles, m. p. 213—214°.

Bouveault's method of converting this α-ketocarboxylic acid into the aldehyde by heating with aniline and then hydrolysing the anil

(Abstr., 1896, i, 649) was used. *Trimethylgallaldehyde*, $C_{10}H_{12}O_4$, crystallises from light petroleum in colourless leaflets, m. p. 74—75°. It has all the usual properties of an aldehyde; its p-*nitrophenylhydrazone*, $C_{16}H_{17}O_5N_3$, forms red needles, m. p. 201—202°, and the *semicarbazone*, $C_{11}H_{15}O_4N_3$, crystallises from water in colourless needles, m. p. 219—220°. W. R.

Formation of Mixtures of Isomerides of Constant Melting Point in Friedel and Crafts' Reaction. GUSTAVE PERRIER and H. CAILLE (*Compt. rend.*, 1908, **146**, 769—770).—One of the authors (Perrier, *Thèse*, Paris, 1896) has described previously a method of separating the mixtures of isomeric ketones obtained by Friedel and Crafts' reaction, based on the differences in stability and solubility in carbon disulphide of their additive compounds with aluminium chloride. To effect a good separation by this method, the crystals first deposited must be collected separately, and when decomposed with water these give one isomeride in a pure state. If in the preparation of the phenyl naphthyl ketones this precaution is not observed, the product consists, not of the β-isomeride, but of a substance, m. p. 54° (sharp), also resulting from Friedel and Crafts' reaction as ordinarily carried out. This substance by (1) recrystallisation from light petroleum and mechanical separation of the crystals deposited, and (2) preparation of the picrates, can be separated into the α- (m. p. 75°) and the β-isomerides (m. p. 82°), and appears to be a eutectic mixture of the two. E. H.

isoOrcacetophenone Dimethyl Ether. JOSEF TAMBOR [and, in part, ST. BARANOWSKI, A. COMTESSE, and W. TOMI] (*Ber.*, 1908, **41**, 793—798. Compare this vol., i, 358).—A substance, obtained occasionally as a by-product in the preparation of orcacetophenone dimethyl ether, is now found to be an isomeride. When heated with methyl benzoate, *m*-methoxybenzoate, or veratrate, and sodium, it forms substituted benzoylacetophenones, which are isomeric with those obtained under the same conditions from orcacetophenone dimethyl ether, and are converted in the same manner into substituted methylflavones. Hence the iso*orcacetophenone dimethyl ether* must have the constitution  $\begin{array}{l}\mathrm{C(OMe){:}CH{\cdot}CMe}\\ \mathrm{CH{:}C(OMe){\cdot}C{\cdot}COMe}\end{array}$. It is prepared by the action of acetyl chloride and aluminium chloride on orcinol dimethyl ether in presence of small amounts of glacial acetic acid, or of acetic anhydride and aluminium chloride on cooled orcinol dimethyl ether; it crystallises on evaporation of the light petroleum filtrate from orcacetophenone dimethyl ether in white needles, m. p. 48°. iso*Orcacetophenone monomethyl ether*, formed together with the dimethyl ether, must be a product of the hydrolysis of this having the constitution



$$\begin{array}{l}\mathrm{C(OMe){:}CH{\cdot}CMe}\\ \mathrm{CH{:}C(OH){-}C{\cdot}COMe}\end{array}$$

since in substituted acetophenones a methoxyl group in the ortho position is always more easily hydrolysed than one in the para position. The monomethyl ether crystallises in white needles, m. p. 79°, and is converted into the dimethyl ether by the action of methyl sulphate and alkalis.

2 : 4-*Dimethoxy*-6-*methylbenzoylacetophenone*,
$C_6H_2Me(OMe)_2\cdot CO\cdot CH_2\cdot COPh$,
crystallises in white needles, m. p. 76—77°, and when boiled with concentrated hydriodic acid yields (*a*) 7-*methoxy*-5-*methylflavone*,
$OMe\cdot C_9H_3O_2PhMe$,
which crystallises in colourless needles, m. p. 115°, and is insoluble in alkalis, and (*b*) 7-*hydroxy*-5-*methylflavone*, $OH\cdot C_9H_3O_2PhMe$, which forms white needles, m. p. 297°, dissolves in dilute sodium hydroxide to a slightly yellow, or in concentrated sulphuric acid to a colourless, solution with blue fluorescence, and is converted by methyl sulphate and alkalis into 7-methoxy-5-methylflavone. 7-*Acetoxy*-5-*methylflavone*, $C_{18}H_{14}O_4$, forms colourless needles, m. p. 147°.

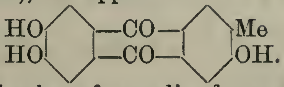
2 : 4 : 3′-*Trimethoxy*-6-*methylbenzoylacetophenone*,
$C_6H_2Me(OMe)_2\cdot CO\cdot CH_2\cdot CO\cdot C_6H_4\cdot OMe$,
prepared from *iso*orcacetophenone dimethyl ether and methyl *m*-methoxybenzoate, crystallises in colourless prisms, m. p. 107°. 7 : 3′-*Dihydroxy*-5-*methylflavone*, $OH\cdot C_9H_3O_2Me\cdot C_6H_4\cdot OH$, colourless needles, m. p. 260°.

2 : 4 : 3′ : 4′-*Tetramethoxy*-6-*methylbenzoylacetophenone*, $C_{20}H_{22}O_6$, prepared from the *iso*dimethyl ether and methyl veratrate, crystallises in white needles, m. p. 134°. 7 : 3′ : 4′-*Trihydroxy*-5-*methylflavone*, $C_{16}H_{12}O_5$, greenish-yellow needles, m. p. 258°. The *triacetate*, $C_{22}H_{18}O_8$, white needles, m. p. 188°.

The di-, tri-, and tetra-methoxymethylbenzoylacetophenones give red colorations with alcoholic ferric chloride. The di- and tri-hydroxymethylflavones form yellow or greenish-yellow solutions in concentrated sulphuric acid. G. Y.

Preparation of Aldehydes and Quinones. Walther Lang (D.R.-P. 189178).—*Manganous ammonium sulphate*,
$2MnSO_4,(NH_4)_2SO_4$,
is obtained from a hot acid solution containing excess of ammonium sulphate; it forms yellow, anhydrous crystals, and is decomposed by water into the double salt, $MnSO_4,(NH_4)_2SO_4$, and ammonium sulphate. The new double salt, dissolved in dilute sulphuric acid, is electrolysed into manganic ammonium alum, a lead-lined electrolytic cell serving as the anode. When benzene and toluene are oxidised with this manganic salt at 50°, *p*-benzoquinone and benzaldehyde are produced, whilst naphthalene, anthracene, and phenanthrene yield their respective quinones. G. T. M.

Trimethyl Ethers of Emodin from Frangula and from Aloes. Otto A. Oesterle and Ed. Tisza (*Arch. Pharm.*, 1908, **246**, 112—116).—The above emodins have been methylated (with methyl sulphate in aqueous solution) with a view to determining whether any of the hydroxyl groups are in the α-position to a carbonyl group, and thus resist methylation (as found by Kostanecki and Drehe. Frangula-emodin readily gives a *trimethyl ether*, $C_{15}H_7O_2(OMe)_3$, yellow needles, m. p. 225°, and, since this emodin is derived from β-methylanthracene (according to Liebermann), it appears to be a 3 : 6 : 7-trihydroxy-2-methylanthraquinone :



The isomeric *trimethyl ether* of emodin from aloës forms orange-coloured needles, m. p. 163°, and is only formed very slowly ; from this and from the tinctorial properties, it is deduced that two, at least, of the hydroxyl groups are in α-positions. The substance thus appears to be connected with chrysazin. G. B.

Preparation of Dimenthyl Dimethylene Ether. K. A. Lingner (D.R.-P. 189331).—Dimenthyl dimethylene ether, $O(CH_2{\cdot}O{\cdot}C_{10}H_{19})_2$, formerly obtained from menthol, formaldehyde, and a mineral acid at low temperatures, has now been prepared by adding *s*-dichloromethyl ether to a toluene solution of sodium menthyl oxide, the yield being 76% of the calculated. G. T. M.

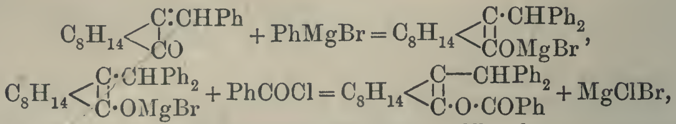
Preparation of Bornyl Borate. Vereinigte Chininfabriken Zimmer & Co. (D.R.-P. 188703).—*Bornyl borate*, $B(OC_{10}H_{17})_3$, a white, tasteless powder, is prepared by heating borneol with boric acid or anhydride in xylene, or by melting together at 250° boryl acetic anhydride and borneol. G. T. M.

Preparation of *iso*Bornyl Esters of the Fatty Acids from Pinene Hydrochloride or Hydrobromide. Chemische Fabrik von Heyden (D.R.-P. 189261).—*iso*Bornyl acetate results from the heating together of pinene hydrochloride, acetic acid, zinc chloride, and aluminium hydroxide or magnesium oxide. The presence of zinc chloride is essential ; in its absence, a portion of the pinene derivative remains unchanged. G. T. M.

Dynamic Isomerism. Henry E. Armstrong, Thomas M. Lowry, Sydney Young, James J. Dobbie, Arthur Lapworth, Martin O. Forster, and Cecil H. Desch (*Brit. Assoc. Report*, 1907, 77, 270—272).—This report deals mainly with the influence of impurities on the velocity of mutarotation of nitrocamphor. T. H. P.

An Isomeride of Diphenylcamphorylmethane and the Conditions of its Formation. Albin Haller and E. Bauer (*Compt. rend.*, 1908, **146**, 718—722).—When diphenylcamphorylmethylene is reduced by sodium amalgam in acid-alcoholic solution, diphenylcamphorylmethane, m. p. 106—107°, is formed (Abstr., 1906, i, 441), but, if the reduction is carried out in alkaline alcoholic solution, an *isomeride*, m. p. 136°, is obtained. The compound described previously is, moreover, transformed into its isomeride when boiled with alcoholic potash, or when heated with sodamide in the presence of toluene.

The product of the action of magnesium phenyl bromide on benzylidenecamphor reacts with benzoyl chloride, as has been described for the benzylideneacetophenone derivative (Kohler Abstr., 1904, i, 595), thus:



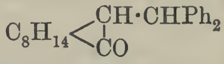
$$C_8H_{14}<\genfrac{}{}{0pt}{}{C{:}CHPh}{CO} + PhMgBr = C_8H_{14}<\genfrac{}{}{0pt}{}{C\cdot CHPh_2}{COMgBr},$$

$$C_8H_{14}<\genfrac{}{}{0pt}{}{C\cdot CHPh_2}{C\cdot OMgBr} + PhCOCl = C_8H_{14}<\genfrac{}{}{0pt}{}{C—CHPh_2}{C\cdot O\cdot COPh} + MgClBr,$$

forming *diphenylcamphorylmethane benzoate.* The latter compound, whether hydrolysed by boiling alcoholic potash, by cold sodium ethoxide solution, by ammonia at 180°, or by concentrated hydrochloric acid at 150°, invariably gives rise to the isomeride, m. p. 136—137°. But the benzoyl derivative cannot be prepared by the direct action of benzoyl chloride on either of the modifications of diphenylcamphorylmethane.

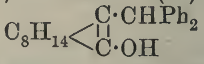
The observed molecular refractive powers of the isomerides, m. p. 106—107° and 136—137°, are 98·39 and 98·87 respectively, whilst the values calculated for the ketonic (I) and enolic (II) forms of

I.



$$C_8H_{14}<\genfrac{}{}{0pt}{}{CH\cdot CHPh_2}{CO}$$

II.



$$C_8H_{14}<\genfrac{}{}{0pt}{}{C\cdot CHPh_2}{C\cdot OH}$$

diphenylcamphorylmethane are 97·35 and 98·29. But, although the observed values approximate to the latter figure, it cannot be deduced that the isomerides have the enolic form, since it has been shown (Haller and Muller, Abstr., 1900, i, 182) that introduction of aromatic groups into the camphor molecule increases the molecular refractive power by as much as one unit.

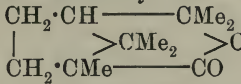
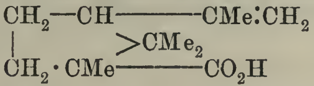
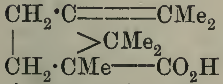
It is stated in conclusion that hitherto no reaction or physical measurement has elucidated the constitution of these two isomeric compounds. E. H.

Preparation of Normal Alkyl Camphorates. J. D. RIEDEL (D.R.-P. 189840).—The methods hitherto employed have not given a satisfactory yield of dialkyl camphorates, as the normal ester was always mixed with the acid ester. It has now been found that the use of alkyl sulphates or aryl sulphonates readily leads to the normal ester.

Methyl *d*-camphorate was obtained by adding methyl sulphate to an alkaline solution of *d*-camphoric acid.

Ethyl *d*-camphorate was prepared either by adding ethyl sulphate to *d*-camphoric acid dissolved in alcoholic sodium ethoxide, or by mixing together ethyl benzenesulphonate and an aqueous solution of potassium *d*-camphorate. G. T. M.

Dimethylcampholide. GUSTAV KOMPPA (*Ber.*, 1908, **41**, 1039—1044).—This investigation had as its object the preparation of *aa*-dimethylcamphor, in order that the properties of this compound might be contrasted with those of fenchone. If the latter compound has the constitution assigned to it by Semmler, then the two substances should closely resemble one another in chemical properties. In order to obtain the dimethylcamphor, dimethylcampholide was first prepared; it was then thought possible that by treating this with potassium cyanide and hydrolysing the cyanide formed, that dimethylhomocamphoric acid would be obtained, from which dimethylcamphor could be prepared by the dry distillation of the calcium salt. This, however, could not be realised, since dimethylcampholide, when heated with potassium cyanide, yields an acid isomeric with dimethylcampholide, instead of the desired cyanide.

Dimethylcampholide,  $\begin{array}{l} CH_2\cdot CH\text{———}CMe_2 \\ |\qquad\quad >CMe_2\quad >O \\ CH_2\cdot CMe\text{———}CO \end{array}$, is prepared by treating with dilute sulphuric acid the additive product formed by acting on camphoric anhydride with magnesium methyl iodide in ether; it crystallises in slender, white needles, m. p. 83·5—85°. When heated alone in a sealed tube at 285—300° or with potassium cyanide at 275—290°, or with 50% aqueous potassium hydroxide solution under pressure at 285—295°, it is converted into an unsaturated monobasic *acid*, which probably has the formula  $\begin{array}{l} CH_2\text{—}CH\text{———}CMe{:}CH_2 \\ |\qquad\qquad >CMe_2 \\ CH_2\cdot CMe\text{———}CO_2H \end{array}$ or  $\begin{array}{l} CH_2\cdot C\text{===}CMe_2 \\ |\qquad >CMe_2 \\ CH_2\cdot CMe\text{—}CO_2H \end{array}$; it crystallises in bent needles, m. p. 68·5—70·5°; the *ammonium* salt crystallises in glistening, white leaflets. The acid decolorises bromine water and potassium permanganate solution, and is reconverted into dimethylcampholide by passing dry hydrogen chloride into its solution in absolute ether. W. H. G.

Sesquiterpene from Oleum Cadinum. IWAN SCHINDELMEISER (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 181—184. Compare Lepeschkin, this vol., i, 278).—The sesquiterpene described by Lepeschkin is considered to be a mixture of a sesquiterpene described by Tröger and Feldmann (Abstr., 1899, i, 376) with considerable quantities of cadinene; and the isomeric sesquiterpene obtained by treating Lepeschkin's substance with hydrogen iodide is not identical with humulene, but consists of a mixture of tetrahydrocadinene, cadinene, and an optically inactive sesquiterpene. Z. K.

Sesquiterpenes. II. ERNST DEUSSEN and ARNOLD LEWINSOHN (*Annalen*, 1908, **359**, 245—261. Compare Abstr., 1907, i, 945).—1. *Caryophyllene Series.*—It is now found that, on repeated distillation, caryophyllene yields two hydrocarbons, one of which has b. p. 132—134°/16 mm., $[\alpha]_D^{20}$ $-4·67°$, D^{20} 0·90346, n_D^{20} 1·49973, and yields 20·8% of nitrosochloride and 8·2% of blue nitrosite, whilst the other has b. p. 128—128·5°/17 mm., $[\alpha]_D^{17}$ $-23·57°$, D^{17} 0·91034, n_D^{17} 1·49899, and yields only traces of nitrosochloride and 0·5% of nitrosite. This hydrocarbon is not identical with the sesquiterpene, b. p. 123—124°/14 mm., previously described (*loc. cit.*), as that forms 25% of nitrosochloride. A further fraction obtained from caryophyllene has $[\alpha]_D$ $-8°$ to $-9·6°$, and gives 4·5—4·0% of nitrosochloride and 19·5—22% of nitrosite. The conclusion is drawn that the caryophyllenes, described in the literature, are mixtures of inactive caryophyllene with considerable amounts of a lævorotatory hydrocarbon.

a-Caryophyllene nitrosobromide, $C_{15}H_{24}ONBr$, prepared by the action of ethereal hydrogen bromide on a mixture of caryophyllene, ethyl nitrite, ethyl acetate, and alcohol at −20°, separates from chloroform in crystals, m. p. 144—145° (decomp.), is optically inactive, and when heated with sodium methoxide yields *i*-*a*-nitrosocaryophyllene, m. p. 116°. With bromine in carbon tetrachloride solution, this forms an *additive* compound, which, on recrystallisation from boiling alcohol, is converted into the optically inactive *bromo-ethoxy*-compound,

$$C_{15}H_{23}Br(NO)\cdot OEt,$$

crystallising in colourless needles, m. p. 185—186° (decomp.).

Caryophyllene nitrosate, m. p. 130·5°, is now found to be optically active, having $[\alpha]_D$ +56·91°. It is formed together with a *substance* crystallising in rosettes, m. p. 156—157°, by the action of chromic acid, equivalent to three atoms of oxygen, on the blue nitrosite in glacial acetic acid solution. When boiled with alcohol, the blue nitrosite yields a dicyclic hydrocarbon, $C_{15}H_{24}$, b. p. 125—125·5°/14·5 mm., D^{19} 0·89941, $[\alpha]_D^{19}$ −26·174°, n_D^{19} 1·49665, which is identical with the sesquiterpene, b. p. 123—124°/14·5 mm., previously described (*loc. cit.*), and forms two isomeric nitrosochlorides; the one of these has m. p. 122°, $[\alpha]_D$ +14·71°, and the other, m. p. 146°, $[\alpha]_D$ −33·69°. Both nitrosochlorides react with benzylamine, forming *β*-caryophyllenenitrolbenzylamine, m. p. 172—173°.

When the hydrocarbon, b. p. 123—124°/14·5 mm., is treated with nitrosyl chloride, the filtrate from the resulting nitrosochloride contains a tricyclic *hydrocarbon*, $C_{15}H_{24}$, b. p. 132—134°/15 mm., D^{18} 0·9310, $[\alpha]_D$ −22·28°, n_D^{18} 1·50085. This forms a white, crystalline *nitrosite*, m. p. 175°.

Clovene, prepared by Wallach and Walker's method (Abstr., 1893, i, 102) for the purpose of comparison with the preceding hydrocarbon, is obtained in two fractions: b. p. 131—139°/15·5 mm., D^{19} 0·92223, α +1·30° (100 mm. tube), n_D^{19} 1·4740, and b. p. 139—143°/15·5 mm., D^{19} 0·92786, α +2·75° (100 mm. tube), n_D^{19} 1·50085, respectively. It does not form a nitrosite, and is probably a mixture.

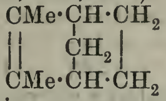
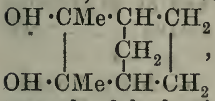
When oxidised with an amount of potassium permanganate, equivalent to four atoms of oxygen in dilute aqueous solution, caryophyllene, $[\alpha]_D$ −14°, obtained from clove oil, yields a *substance*, $C_{15}H_{22}O_4$, which crystallises in needles and leaflets, m. p. 120·5°, is strongly lævorotatory, has a persistent bitter taste, and appears to be derived from the lævorotatory hydrocarbon.

II. *Cadinene.*—If a current of chlorine is passed through a cooled solution of *l*-cadinene dihydrochloride exposed to sunlight, hydrogen chloride is evolved, and, on evaporation of the product, a white, sandy *powder*, $C_{15}H_{20}Cl_8$ or $C_{15}H_{18}Cl_8$, m. p. 65—70°, is obtained. This is probably a mixture of chloro-compounds, which cannot crystallise in presence of each other (compare Gladstone and Hibbert, Abstr., 1889, 1207).

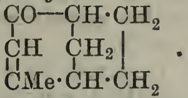
The action of bromine on cadinene dihydrobromide in presence of a small amount of mercuric chloride leads to the formation of a grey, amorphous *powder*, $C_{15}H_{23}Br_5$, m. p. about 100° (evolving hydrogen bromide). G. Y.

Long Leaf Pine Oil. JOHN E. TEEPLE (*J. Amer. Chem. Soc.*, 1908, 30, 412—414).—Long leaf pine oil, obtained by the distillation of lightwood (*Pinus palustris*) with steam, has a faint yellow colour, $D^{15 \cdot 5}$ 0·935—0·947, $[\alpha]_D$ about −11°, and n_D 1·483. When heated, it begins to distil at about 206—210°; 75% collects between 211° and 218°, and 50% between 213° and 217°. The sp. gr. of the distillate increases regularly as the temperature rises, and becomes steady at about 0·947 at 217°. The oil consists essentially of terpineol, probably the *l*-modification of α-terpineol [Δ^1-*p*-menthenol-(8)] of b. p. 217—218°.

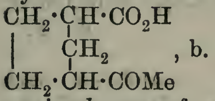
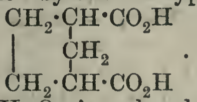
E. G.

Constituents of Essential Oils. Derivatives of Santene, Santene Glycol, and the Unsaturated Ketone, $C_9H_{12}O$, derived from the Diketone, $C_9H_{14}O_2$. FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1908, 41, 866—871. Compare Abstr., 1907, i, 1062; this vol., i, 38, 194, 195).—When the unsaturated dicyclic hydrocarbon santene,  $\begin{array}{l} CMe\cdot CH\cdot CH_2 \\ \| \qquad CH_2 \,| \\ CMe\cdot CH\cdot CH_2 \end{array}$, dissolved in diluted acetone, is oxidised by potassium permanganate, it yields a *glycol*,  $\begin{array}{l} OH\cdot CMe\cdot CH\cdot CH_2 \\ | \qquad\qquad CH_2 \,| \\ OH\cdot CMe\cdot CH\cdot CH_2 \end{array}$, m. p. 193°, b. p. 135°/10 mm., which is very stable towards dehydrating agents and is converted by boiling dilute sulphuric acid into a *ketone*, $C_9H_{14}O$, b. p. 76—80°/10 mm., D^{20} 0·988, n_D 1·47980, which is not identical with camphenilone.

Oxidation of the glycol yields the saturated ketone, $C_9H_{14}O_2$, described previously, from which the unsaturated ketone, $C_9H_{12}O$, formerly obtained by the action of sodium ethoxide, is prepared in very much better yield by the action of alcoholic ammonia at 170°. This unsaturated ketone, b. p. 104—105°/10 mm., D^{20} 1·029, n_D 1·51390, is not a derivative of di*cyclo*-2 : 2 : 2-octane, as stated previously, but is 1-methyldi*cyclo*-1 : 2 : 3-Δ^1-octene-3-one,



$$\begin{array}{l} CO{-}CH\cdot CH_2 \\ CH \quad CH_2 \,| \\ CMe\cdot CH\cdot CH_2 \end{array}.$$

By oxidation with potassium permanganate, it yields the *ketonic acid*,  $\begin{array}{l} CH_2\cdot CH\cdot CO_2H \\ | \qquad CH_2 \\ CH_2\cdot CH\cdot COMe \end{array}$, b. p. 173—175°/10 mm, D^{20} 1·150, n_D 1·47936, the *semicarbazone* of which has m. p. 182°. The constitution of the ketonic acid is proved by its oxidation by sodium hypobromite to *cis*-*cyclo*pentane-1 : 3-dicarboxylic acid,  $\begin{array}{l} CH_2\cdot CH\cdot CO_2H \\ | \qquad CH_2 \\ CH_2\cdot CH\cdot CO_2H \end{array}$.

The dioxime of the ketone, $C_9H_{14}O_2$, is reduced by sodium and alcohol to a *base*, $C_9H_{17}N$, b. p. 78—80°/10 mm., D^{20} 0·953, n_D 1·49856, the *picrate* of which has m. p. 192°.

C. S.

Resin Oil. WILLI SCHULTZE (*Annalen*, 1908, **359**, 129—144).—The crude oil, obtained in a yield of about 60% on further distillation of American colophony after the resin essence, which forms about 5% of the resin, and the light oil, amounting to about 10%, have been removed, has been investigated by a number of authors, who have disagreed as to whether it is a simple substance or a mixture of hydrocarbons. A refined resin oil, obtained in a 60% yield on fractional distillation of the crude oil, is now found to be a mixture of saturated and unsaturated hydrocarbons. It is a wine-yellow liquid, having a strong violet fluorescence, b. p. about 300—350°, D^{15} 0·9693, α_D $-39{\cdot}96°$ (100 mm. tube), has the ignition temperature 112°, the tenacity factor 6·97, and Engler's viscosity factor 2·12 at 50°. At $-20°$, it forms a viscid syrup, solidifies to a vitreous mass in a carbon dioxide-ether mixture, and distils unchanged under 12 mm. pressure, but evolves gas on prolonged boiling in a reflux apparatus. A pure substance could not be obtained by fractional distillation or solidification.

On treatment of the refined oil with concentrated sulphuric acid and repeated distillation of the product over sodium, a mixture of saturated hydrocarbons is obtained in a 36% yield as a transparent liquid, which has an odour faintly resembling petroleum, is not fluorescent, is stable towards alkaline permanganate or bromine water, and on distillation yields four fractions: b. p. 152—179°/10 mm., D^{15} 0·9486, α_D $-3{\cdot}23°$ (100 mm. tube); b. p. 178·5—189°/10 mm., D^{15} 0·9550, α_D $-4{\cdot}14°$; b. p. 191—194°/13·5 mm., D^{15} 0·9590, α_D $-10{\cdot}66°$, and b. p. 196—202°/13·5 mm., D^{15} 0·9780, α_D $-20{\cdot}22°$, respectively. A fraction, b. p. 195—197·5°/19 mm., gave on analysis figures agreeing only approximately with those required by octahydroretene. When boiled with manganese dioxide and dilute sulphuric acid, the saturated oil yields trimellitic acid and a saturated *hydrocarbon*, b. p. 198·5—200°/18·5—20 mm., which is volatile with steam and is not attacked by fuming sulphuric acid. The action of sulphur on the saturated oil, b. p. 178—210°/11—12 mm., leads to the formation of retene, m. p. 98·5—99°, and a *substance*, $C_{18}H_{16}S$, which is formed also by heating retene with sulphur at 230—240°. It crystallises in white leaflets, m. p. 225·5—226°, and gives an intense indigo-blue coloration with a mixture of fuming and concentrated sulphuric acids.

Trimellitic acid is best prepared by oxidation of ψ-cumene with potassium permanganate in boiling aqueous sodium hydroxide solution; the anhydride has m. p. 162·5—163° (157—158°: Baeyer, this Journ., 1873, 756). G. Y.

Arbutin and Some of its Derivatives considered with Regard to their Rotatory Power and their Hydrolysis by Emulsin. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1908, **146**, 764—766*).—Pure arbutin, that is, a glucoside which on hydrolysis gives one molecule of dextrose and one molecule of quinol, has not yet been obtained. According to Schiff and others, commercial arbutin is a mixture of arbutin (as above defined) and methylarbutin, whilst Habermann holds that arbutin is a complex glucoside, $C_{25}H_{34}O_{14}$, containing the elements dextrose, quinol, and quinol methyl ether. By a cryoscopic determination, the authors have found the value 268 for the molecular weight of the commercial glucoside, which is so nearly in accordance with the number 272 required by $OH\cdot C_6H_4\cdot O\cdot C_6H_{11}O_5$ as to render Habermann's theory untenable. Undried commercial arbutin has α_D −61·76°, which becomes −61·3° after purification. The purified glucoside loses 5·15% of water when dried at 120—125°, from which the value α_D −64·7° is deduced for the dry substance.

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* and *J. Pharm. Chim.*, 1908, **27**, 421—427.

Arbutin methyl ether, prepared according to Schiff's directions, has m. p. 175—176° (corr.) and α_D −63·43°. Since the latter is very close to the value for purified arbutin, the specific rotatory power of true arbutin must approximate to −65°, and thus the glucoside is lævorotatory.

Arbutin benzyl ether, $CH_2Ph\cdot O\cdot C_6H_4\cdot O\cdot C_6H_{11}O_5$, has m. p. 161—162° and α_D^{17} −44·47° (in alcohol). Dinitroarbutin, $OH\cdot C_6H_2(NO_2)_2\cdot O\cdot C_6H_{11}O_5$, is lævorotatory. The compounds, arbutin methyl and benzyl ethers and dinitroarbutin, are hydrolysed by emulsin.

The conclusion is drawn that arbutin and its three derivatives follow the rule laid down by the authors that "all glucosides hydrolysed by emulsin are lævorotatory and are derived from dextrose." E. H.

Simple Method of Preparation of Phylloporphyrin. LEON MARCHLEWSKI [with PIASECKI] (*Ber.*, 1908, **41**, 847—849*).—To prepare phylloporphyrin it is no longer first necessary to isolate phyllotaonin; the following method renders the former compound one of the easiest chlorophyll derivatives to prepare. A slight excess of barium hydroxide is added to an extract of dried acacia leaves. The precipitate is separated, washed, suspended in 96% alcohol, and carefully decomposed with concentrated sulphuric acid. The slightly acid solution is concentrated and heated with 10% alcoholic potash in an autoclave at 200°. The product is neutralised with acetic acid and warmed with alcohol, whereon phylloporphyrin dissolves, leaving a brown residue. The alcohol is evaporated, water added, and the phylloporphyrin and other chlorophyll derivatives extracted with ether. The ethereal solution is shaken with 5% hydrochloric acid, and the phylloporphyrin precipitated from this in the form of a reddish-brown mud by sodium acetate. This is dissolved in ether and the above process repeated, using 1% hydrochloric acid. The product is recrystallised twice from alcohol, and obtained as bright brown, narrow, rhombic plates pointed at both ends. E. F. A.

An Attempt to Synthesise 1 : 2-Coumaran. MAXIMILIAN HELBIG (*J. pr. Chem.*, 1908, [ii], **77**, 364—366).—The sodium derivative of salicylaldehyde is most readily prepared by adding the theoretical amount of sodium ethoxide solution gradually to the aldehyde dissolved in three times its weight of absolute alcohol.

When the sodium derivative is heated with bromosuccinic acid, hydrogen bromide is eliminated and fumaric acid formed. The sodium derivative condenses with ethylene dibromide at 130—140°, yielding the *bromoethyl ether* of salicylaldehyde,

$$CH_2Br\cdot CH_2\cdot O\cdot C_6H_4\cdot CHO.$$

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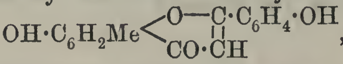
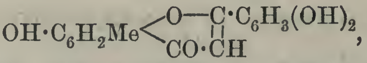
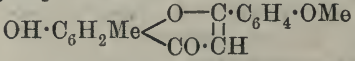
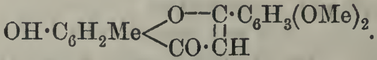
* *Bull. Acad. Sci. Cracow*, 1908, **3**, 127—129.

It has m. p. 52°, b. p. 184°/11—12 mm., and gives a red coloration with ferric chloride.

The *phenylhydrazone*, $C_{15}H_{15}ON_2Br$, crystallises in yellow needles, m. p. 114°.

Further condensation to the coumaran does not occur. J. J. S.

The Flavone Group. Josef Tambor [and, in part, B. Aronstamm, St. Baranowski, St. Cukier, and W. Tomi] (*Ber.*, 1908, **41**, 787—792).—Tambor and Ludwinowsky found that orcacetophenone dimethyl ether condenses with ethyl benzoate, forming 2 : 6-dimethoxy-4-methylbenzoylacetophenone (Abstr., 1907, i, 75), which when boiled with hydriodic acid, D 2·00, yields 1-hydroxy-3-methylflavone. This reaction has now been extended to the condensation of orcacetophenone with the three methyl methoxybenzoates and with methyl veratrate, which form the corresponding 2 : 6-dimethoxy-4-methylbenzoyl-methoxyacetophenones, $C_6H_2Me(OMe)_2\cdot CO\cdot CH_2\cdot CO\cdot C_6H_4\cdot OMe$, and -dimethoxyacetophenone, $C_6H_2Me(OMe)_2\cdot CO\cdot CH_2\cdot CO\cdot C_6H_3(OMe)_2$. These are converted by treatment with hydriodic acid, D 2·00, into the dihydroxy-,  $OH\cdot C_6H_2Me{<}\begin{array}{l}O{-}C\cdot C_6H_4\cdot OH\\ \quad\;\, \|\\ CO\cdot CH\end{array}$, and trihydroxy-7-methylflavones,  $OH\cdot C_6H_2Me{<}\begin{array}{l}O{-}C\cdot C_6H_3(OH)_2\\ \quad\;\, \|\\ CO\cdot CH\end{array}$, respectively. When these are heated with potassium hydroxide and methyl iodide, the hydroxyl in position 5 remains unchanged, but the hydroxyls in the phenyl group are etherified, the resulting ethers having the constitution  $OH\cdot C_6H_2Me{<}\begin{array}{l}O{-}C\cdot C_6H_4\cdot OMe\\ \quad\;\, \|\\ CO\cdot CH\end{array}$ or  $OH\cdot C_6H_2Me{<}\begin{array}{l}O{-}C\cdot C_6H_3(OMe)_2\\ \quad\;\, \|\\ CO\cdot CH\end{array}$.

The results of the work now published confirm the view of Tambor and Ludwinowsky (*loc. cit.*) as to the constitution of orcacetophenone.

Orcacetophenone dimethyl ether crystallises in rhombic plates [$a : b : c = 0{\cdot}7522 : 1 : 0{\cdot}3932$].

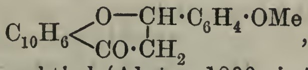
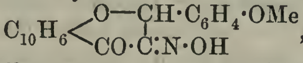
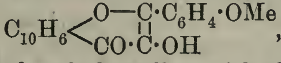
2 : 6 : 2′-*Trimethoxy-4-methylbenzoylacetophenone*, $C_{19}H_{20}O_5$, prepared from methyl methylsalicylate, crystallises in rose-coloured needles, m. p. 118°, and gives a blood-red coloration with ferric chloride. 5 : 2′-*Dihydroxy-7-methylflavone*, $C_{16}H_{12}O_4$, forms greenish-yellow needles, m. p. 300—301°; the *diacetate*, $C_{20}H_{16}O_6$, white prisms, m. p. 108°. 5-*Hydroxy-2′-methoxy-7-methylflavone*, $C_{17}H_{14}O_4$, crystallises in yellow needles, m. p. 156°, and forms a sparingly soluble, yellow *sodium* salt.

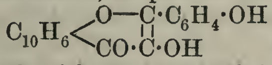
2 : 6 : 3′-*Trimethoxy-4-methylbenzoylacetophenone*, prepared from methyl *m*-methoxybenzoate, crystallises in light brown prisms, m. p. 98°. 5 : 3′-*Dihydroxy-7-methylflavone* forms colourless needles, m. p. 227°, and forms a yellow solution in concentrated sulphuric acid, but does not dye mordanted threads; the *diacetate* crystallises in yellow, rhombic prisms, m. p. 137°. 5-*Hydroxy-3′-methoxy-7-methylflavone* forms yellow needles, m. p. 146°, yields a sparingly soluble, yellow *sodium* salt, and gives a yellow coloration with concentrated sulphuric acid.

2 : 6 : 4′-*Trimethoxy-4-methylbenzoylacetophenone*, prepared from methyl anisate, crystallises in colourless needles, m. p. 97—98°. 5 : 4′-Dihydroxy-7-methylflavone crystallises from alcohol in yellow needles, m. p. 295°; the *diacetate*, white needles, m. p. 148—149°. 5-*Hydroxy*-4′-*methoxy*-7-*methylflavone* crystallises in yellow needles, m. p. 274°, and forms an insoluble, yellow *sodium* salt.

2 : 6 : 3′ : 4′-*Tetramethoxy*-4-*methylbenzoylacetophenone*, $C_{20}H_{22}O_6$, from methyl veratrate, crystallises in white needles, m. p. 112°. 5 : 3′ : 4′-*Trihydroxy*-7-*methylflavone*, $C_{16}H_{12}O_5$, yellow needles, m. p. 270°, gives with concentrated sulphuric acid a light yellow, or with sodium hydroxide solution an intense yellow coloration, and alumina mordant dyes a greenish-yellow. The *triacetate*, $C_{22}H_{18}O_8$, forms white needles, m. p. 169°. 5-*Hydroxy*-3′ : 4′-*dimethoxy*-7-*methylflavone*, $C_{18}H_{16}O_5$, crystallises in yellow needles, m. p. 147°, forms an insoluble, yellow *sodium* salt, and gives a yellow coloration with concentrated sulphuric acid.
G. Y.

Two Monohydroxy-α-naphthaflavonols. STANISLAUS VON KOSTANECKI [and, in part, J. W. ENGELSOHN and M. WURZELMANN] (*Ber.*, 1908, 41, 783—786).—In connexion with Bigler and Kostanecki's investigation of 3′ : 4′-dihydroxy-α-naphthaflavonol (Abstr., 1907, i, 76), 3′- and 4′-hydroxy-α-naphthaflavonols have been prepared and are now described.

4′-*Methoxy-α-naphthaflavanone*,  $C_{10}H_6{<}\begin{array}{l}O—CH\cdot C_6H_4\cdot OMe\\ CO\cdot CH_2\end{array}$, prepared by boiling 2-anisylideneacetyl-1-naphthol (Abstr., 1899, i, 524) with hydrochloric acid in alcoholic solution, crystallises in white needles, m. p. 148°. The iso*nitroso*-derivative,  $C_{10}H_6{<}\begin{array}{l}O—CH\cdot C_6H_4\cdot OMe\\ CO\cdot C{:}N\cdot OH\end{array}$, crystallises from benzene in yellow needles, m. p. 169—170° (decomp.), and dyes orange with cobalt, but yellow with uranium, cadmium, and lead mordants. When boiled with 10% sulphuric acid in glacial acetic acid solution, the *iso*nitroso-derivative is converted into 4′-methoxy-α-naphthaflavonol,  $C_{10}H_6{<}\begin{array}{l}O—C\cdot C_6H_4\cdot OMe\\ CO\cdot C\cdot OH\end{array}$, which crystallises in yellow needles, m. p. 249°, dyes light yellow with alumina mordants, dissolves in concentrated sulphuric acid to a solution with intense light green fluorescence, and forms an insoluble, yellow *sodium* salt. The *acetate*, $OMe\cdot C_{19}H_{10}O_2\cdot OAc$, forms white needles, m. p. 196°.

4′-*Hydroxy-α-naphthaflavonol*,  $C_{10}H_6{<}\begin{array}{l}O—C\cdot C_6H_4\cdot OH\\ CO\cdot C\cdot OH\end{array}$, prepared by boiling the 4′-methoxy-compound with concentrated hydriodic acid, crystallises in yellow plates, m. p. 293°, dyes light yellow with alumina mordants, and dissolves in concentrated sulphuric acid or dilute sodium hydroxide to yellow solutions with green fluorescence. The *diacetate*, $C_{19}H_{10}O_2(OAc)_2$, forms white needles, m. p. 181°.

The members of the isomeric series are prepared in the same manner, starting from 2-m-*methoxybenzylideneacetyl*-1-*naphthol*,

$$OH\cdot C_{10}H_6\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot OMe,$$

which is prepared by condensation of *m*-methoxybenzaldehyde with

2-acetyl-1-naphthol in the usual way. It crystallises in orange-red needles, m. p. 115°, and gives a red coloration with concentrated sulphuric acid.

3′-*Methoxy-α-naphthaflavanone* forms white needles, m. p. 130°. The iso*nitroso*-derivative is a yellow, crystalline powder, m. p. 151° (decomp.), which dyes orange with cobalt mordants. 3′-*Methoxy-α-naphthaflavonol*, yellow needles, m. p. 185°, dyes light yellow with alumina mordants, and forms a yellow *sodium* salt; the *acetate*, white needles, m. p. 165°.

3′-*Hydroxy-α-naphthaflavonol* crystallises from alcohol in yellow, prismatic needles containing C_2H_6O, m. p. 248°, dyes light yellow with alumina mordants, and forms yellow solutions with green fluorescence in concentrated sulphuric acid or very dilute alkalis; the *sodium* salt forms yellow needles. G. Y.

Some Derivatives of Thiophen. VICTOR THOMAS (*Compt. rend.*, 1908, **146**, 642—645).—In the presence of anhydrous ether, magnesium dissolves in 1-iodothiophen, giving magnesium thiophen iodide, which in general behaves like the corresponding phenyl derivative. With the aliphatic ketones, acetone, methyl ethyl ketone, methyl amyl ketone, and butyrone it reacts normally, giving tertiary alcohols, but the latter are difficult to isolate in a pure state, owing to the readiness with which they undergo dehydration, forming ethylenic hydrocarbons. Since the carbinol formed from acetophenone readily loses water, whilst the compound derived from benzophenone is remarkably stable, this dehydration is probably to be represented thus:

$$C_4SH_3\cdot CR(OH)\cdot CH_3 \longrightarrow C_4SH_3\cdot CR\colon CH_2,$$

R signifying an aliphatic or aromatic radicle. Acetone condenses with magnesium thiophen iodide, giving a mixture of *thienyldimethylcarbinol*, $C_4SH_3\cdot CMe_2\cdot OH$, needles, m. p. 33°, which after a time liquefy to a viscous substance with a piquant odour, and *β-thienylpropylene*, $C_4SH_3\cdot CMe\colon CH_2$, a colourless, agreeably smelling liquid, b. p. 166—167°/727 mm., which is easily polymerised when kept, finally giving a solid black mass. Methyl ethyl ketone gives a mixture of alcohol and hydrocarbon which could not be separated. The chief product of the action of methyl amyl ketone on magnesium thiophen iodide is *β-thienylheptylene*, $C_5H_{11}\cdot C(C_4SH_3)\colon CH_2$, a somewhat oily liquid, b. p. 165—168°/62 mm. Butyrone gives *thienyldipropylcarbinol*, $C_4SH_3\cdot CPr_2\cdot OH$, an agreeably smelling liquid, b. p. 160—163°/45—46 mm., which on distillation at ordinary pressure decomposes into the hydrocarbon and water. Acetophenone forms *α-phenyl-α-thienylmethylcarbinol*, $C_4SH_3\cdot CPhMe\cdot OH$, needles, m. p. 50°, which gradually undergo partial liquefaction, probably forming the hydrocarbon. *Diphenylthienylcarbinol*, $C_4SH_3\cdot CPh_2\cdot OH$, hexagonal crystals, m. p. 125°, is formed from benzophenone; whilst yielding colourless solutions in neutral solvents, it resembles triphenylcarbinol in giving intensely yellow solutions in acids. E. H.

Preparation of 3-Hydroxy-(1)-thionaphthen. KALLE & Co. (D.R.-P. 188702).—It was formerly shown that phenylthioglycol-*o*-carboxylic acid when heated with sodium hydroxide gave 3-hydroxy-(1)-thionaphthen-2-carboxylic acid, which subsequently furnished

3-hydroxy-(1)-thionaphthen. It it now found that the two reactions can be effected in one stage by heating phenylthioglycol-*o*-carboxylic acid at 230°. G. T. M.

Acid Properties of Amino-ketones. Paul Rabe and Wilhelm Schneider (*Ber.*, 1908, **41**, 872—878. Compare Willstätter and Bode, Abstr., 1900, i, 245; Miller and Rohde, Abstr., 1901, i, 95; Rabe, Abstr., 1907, i, 954; this vol., i, 100).—The amphoteric character of the α-, β-, and ϵ-amino-ketones, cinchoninone, piperidylacetophenone, dimethylaminocamphor, tropinone, and cinchotoxine is manifested, not only by the greater solubility (and the change of colour) in dilute sodium hydroxide than in water, but also in the formation of *O*-benzoyl derivatives. The two criteria are more pronounced in the methiodides than in the amino-ketones themselves.

The sodium *salt* of cinchoninone, $C_{19}H_{19}ON_2Na$, is obtained in clusters of yellowish-red crystals by the addition of ether to cinchoninone dissolved in a normal solution of sodium ethoxide; the sodium *salt* of cinchoninone methiodide, $C_{20}H_{22}ON_2INa$, obtained in a similar manner, forms deep yellow crystals.

[With Fritz Braasch.]—Piperidylacetophenone (compare Schmidt and van Ark, Abstr., 1900, i, 686), b. p. 180—181°/26 mm., is a colourless oil with a pronounced basic odour; the *hydrochloride*,

$$C_{13}H_{17}ON,HCl,$$

has m. p. 223°.

Piperidylacetophenone (2 mols.) and benzoyl chloride (1 mol.) in benzene solution deposit after fourteen days nearly the theoretical quantity of the hydrochloride; the *O*-benzoyl derivative, obtained as an oil after evaporation of the solvent, yields by hydrolysis benzoic acid and the products of the decomposition of piperidylacetophenone. Piperidylacetophenone methiodide by treatment with benzoyl chloride and normal sodium hydroxide yields the colourless *benzoyl* derivative, $C_{21}H_{24}O_2NI$, m. p. 146° (decomp.).

Dimethylaminocamphor methiodide, by the Schotten-Baumann method, yields a *benzoyl* derivative, $C_{20}H_{28}O_2NI$.

Tropinone methiodide, m. p. 273—275° (Willstätter gives m. p. 263—265°), forms a *benzoyl* derivative, $C_{16}H_{20}O_2NI$, m. p. 263—265°, which separates from alcohol in rhombic leaflets.

Methylcinchotoxine is more soluble in water than in normal sodium hydroxide. Methylcinchotoxine methiodide is not appreciably more soluble in dilute alkali than in water, but the change of colour in the alkaline solution is an indication of salt formation. It forms a *benzoyl* derivative, $C_{28}H_{31}O_2N_2I$. C. S.

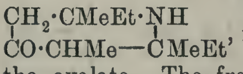
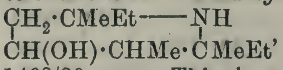
Morphine. XVIII. Hydrolytic Products of α- and β-Chlorocodide. Ludwig Knorr and Heinrich Hörlein (*Ber.*, 1908, **41**, 969—975. Compare Schryver and Lees, Trans., 1900, **77**, 1024; 1901, **79**, 563; Lees and Tutin, Proc., 1906, **22**, 253; Lees, Trans., 1907, **91**, 1408; Knorr and Hörlein, this vol., i, 41).—The following constants for the halogen derivatives of morphine and codeine are given: α-Chloromorphide, m. p. 204° (decomp.); $[\alpha]_D$ $-375°$. β-Chloromorphide, m. p. 188°; $[\alpha]_D$ $-5°$. α-Chlorocodide, m. p. 152—153°;

$[\alpha]_D$ −380°. *β*-Chlorocodide, m. p. 152—153°; $[\alpha]_D$ −10°. Bromomorphide, m. p. 169—170°; $[\alpha]_D$ +66°. Bromocodide, m. p. 162°; $[\alpha]_D$ +56°.

When hydrolysed by boiling with dilute acetic acid, the two chlorocodides yield the same products, but in different proportions. *α*-Chlorocodide gives *ψ*-codeine, 45%; *allo-ψ*-codeine (*β-iso*codeine), 15%, and *iso*codeine, 25%, whereas *β*-chlorocodide gives *ψ*-codeine, 10%; *allo-ψ*-codeine, 20%, and *iso*codeine, 55%. J. J. S.

Hydrolytic Products of α-Chloromorphide. ALFRED OPPÉ (*Ber.*, 1908, **41**, 975—981. Compare Schryver and Lees, Trans., 1900, **77**, 1024; 1901, **79**, 563; Lees, 1907, **91**, 563; Knorr and Hörlein, preceding abstract).—*α*-, *β*-, and *γ-iso*morphines are obtained by the hydrolysis of *α*-chloromorphide with dilute acetic acid. *γ-iso*Morphine (neo*iso*morphine) is readily separated from the *β*-isomeride by extraction with boiling acetone, in which the *γ*-compound is very sparingly soluble. It separates from acetone in compact crystals, and has m. p. 278° (decomp.) and $[\alpha]_D^{15}$ −94°. The hydrochloride has m. p. 314° (decomp.) and $[\alpha]_D^{15}$ −76° (Lees: −79·1°). The *hydrobromide*, $C_{17}H_{20}O_3NBr$, decomposes at 298°, and has $[\alpha]_D^{15}$ −71°. Its *acetyl* derivative is oily, but yields a *methiodide*, $C_{22}H_{26}O_5NI$, which crystallises in needles, m. p. 267° (decomp.) and $[\alpha]_D^{15}$ −24°.

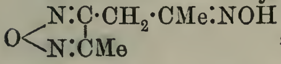
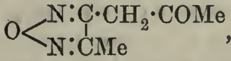
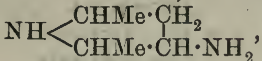
The *methiodide* of diacetylmorphine crystallises in needles, decomposes at 252°, and has $[\alpha]_D^{15}$ −107°. When methylated, *γ-iso*morphine yields *ψ*-codeine, and from this *ε*-methylmorphimethine (Knorr and Hörlein, Abstr., 1907, i, 151) has been obtained. J. J. S.

Action of Ammonia on Methyl Ethyl Ketone. WILHELM TRAUBE (*Ber.*, 1908, **41**, 777—782).—Sokoloff and Latschinoff (this Journ., 1875, 353) found that acetone reacts with ammonia, forming diacetoneamine, together with small amounts of triacetoneamine. The present author has studied the action of ammonia on the first homologue of acetone, methyl ethyl ketone. This absorbs ammonia in only very small amounts, but, if an alcoholic solution of the ketone is saturated with ammonia and allowed to remain at the ordinary temperature for two or three weeks, 4-*keto*-2 : 3 : 6-*trimethyl*-2 : 6-*diethylpiperidine*,  $\begin{array}{l}CH_2\cdot CMeEt\cdot NH \\ CO\cdot CHMe—CMeEt\end{array}$, is formed in a 25% yield, and can be isolated as the oxalate. The free base is a colourless liquid, b. p. 157—159°/30 mm., or 247°/760 mm., and has a characteristic odour. The *nitrate*, $C_{12}H_{23}ON,HNO_3$, crystallises in colourless needles, m. p. 169—172° (decomp.). Reduction of the keto-base by alternate additions of sodium amalgam and dilute hydrochloric acid to the oxalate leads to the formation of 4-*hydroxy*-2 : 3 : 6-*trimethyl*-2 : 6-*diethylpiperidine*,  $\begin{array}{l}CH_2\cdot CMeEt—NH \\ CH(OH)\cdot CHMe\cdot CMeEt\end{array}$, which is obtained as a colourless oil, b. p. 140°/20 mm. This is a mixture of two isomerides, which can be separated by means of the difference in the solubilities of their oxalates. The more sparingly soluble *oxalate*, $C_{12}H_{25}ON,C_2H_2O_4$, m. p. 208° (decomp.), when heated with benzoyl chloride at 160°

yields the *hydrochloride* of the benzoate, $C_{19}H_{29}O_2N,HCl$, m. p. 230°; the *benzoate*, $C_{19}H_{29}O_2N$, forms a colourless oil, which is partially decomposed on distillation in a vacuum, and forms, in addition to the preceding salt, a second highly soluble *hydrochloride*, obtained as a brittle mass on evaporation of the aqueous solution. The base, corresponding with the more soluble oxalate, is converted into the benzoate hydrochloride, m. p. 230°, when heated with benzoyl chloride.

G. Y.

Nitrosopyrroles. E. Morelli and Guerriero Marchetti (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 250—254).—The authors have studied the reactions of the trioxime, $NOH{:}CMe{\cdot}CH_2{\cdot}C(NOH){\cdot}CMe{:}NOH$, obtained by Angeli and Marchetti (Abstr., 1907, i, 436) by the action of hydroxylamine on 3-nitroso-2:5-dimethylpyrrole or 3-nitroso-1-oxy-2:5-dimethylpyrrole.

The trioxime readily loses $1H_2O$, giving a furazan derivative,  $O<\begin{array}{l}N{:}C{\cdot}CH_2{\cdot}CMe{:}NOH\\ N{:}CMe\end{array}$, and this, when boiled with dilute sulphuric acid, yields hydroxylamine and the *ketone*,  $O<\begin{array}{l}N{:}C{\cdot}CH_2{\cdot}COMe\\ N{:}CMe\end{array}$, which crystallises from ether in white needles, m. p. 19°, gives iodoform when treated with potassium hydroxide and iodine, and yields a *semicarbazone*, $C_6H_8ON_2{:}N_2H{\cdot}CO{\cdot}NH_2$, m. p. 188°. When reduced by means of sodium in alcoholic solution, the trioxime yields 3-*amino*-2:5-*dimethylpyrrolidine*,  $NH<\begin{array}{l}CHMe{\cdot}CH_2\\ CHMe{\cdot}CH{\cdot}NH_2\end{array}$, which forms a *picrate*, $C_6H_{14}N_2,2C_6H_3O_7N_3$, m. p. 242° (decomp.).

T. H. P.

Action of Hydrazine Hydrate on Dinitrophenylpiperidine. Leopold Spiegel (*Ber.*, 1908, 41, 886—888).—Hydrazine hydrate in boiling alcoholic solution hydrolyses 2:4-dinitrophenylpiperidine, the products being a piperidine salt and a substance, $C_6H_4O_3N_4$, m. p. 206° (decomp.), crystallising in yellowish-brown, glistening prisms, which is identical with Curtius and Mayer's 6-nitro-1-hydroxy-1:2:3-benzotriazole (this vol., i, 53).

C. S.

***Bz*-Quinoline Mercaptans.** Albert Edinger (*Ber.*, 1908, 41, 937—943).—Quinoline-8-mercaptans have been prepared by the reduction of the corresponding quinolinesulphonyl chlorides with stannous chloride and hydrochloric acid.

Quinoline-8-*sulphonyl chloride*, $C_9NH_6{\cdot}SO_2Cl$, m. p. 122°, prepared from phosphorus pentachloride and the sulphonic acid or its sodium salt at 136—140°, is reduced by stannous chloride and hydrochloric acid, yielding a *double* salt of tin and the mercaptan, which crystallises in stout, yellow prisms and decomposes at 270°. A cold alkaline solution of the double salt with benzoyl chloride yields the *benzoyl* derivative, $C_9NH_6{\cdot}S{\cdot}COPh$, m. p. 110°, whilst benzyl chloride gives the *benzyl* derivative, $C_{16}H_{13}NS$, m. p. 112°. By hydrolysis with hot moderately concentrated hydrochloric acid and subsequent neutralisation at 0°, the benzoyl derivative yields the *mercaptan*, $C_9NH_6{\cdot}SH,2H_2O$, m. p. 58—59°, which crystallises in glistening, red needles. By prolonged exposure to the air or by oxidation with alkaline potassium ferricyanide, the mercaptan yields the *disulphide*, $C_{18}H_{12}N_2S_2$ m. p. 206°, which separates from alcohol or glacial acetic acid in yellow prisms.

8-*Thiocyanoquinoline*, $C_9NH_6{\cdot}SCN$, m. p. 89°, prepared from the mercaptan, sodium methoxide, and cyanogen iodide in methyl-alcoholic solution, separates from dilute alcohol in white needles, and by warming with aniline forms a *substance*, $C_{16}H_{13}N_3S$, m. p. 142°. The *ethyl thio-ether*, $C_9NH_6{\cdot}SEt$, m. p. 51°, crystallises in colourless needles.

5-Bromoquinoline, when heated at 130—140° with fuming sulphuric acid (40% SO_3), yields 5-bromoquinoline-8-sulphonic acid, the *chloride* of which, m. p. 124°, yields by reduction a tin double salt, from which a *benzoyl* derivative, $C_9NH_5Br{\cdot}S{\cdot}COPh$, m. p. 115°, is obtained. The corresponding *mercaptan*, $C_9NH_5Br{\cdot}SH$, m. p. 69°, crystallises in yellow needles. The *disulphide* has m. p. 193°. C. S.

Partial Racemism. VII. Albert Ladenburg and W. Herrmann (*Ber.*, 1908, **41**, 966—969. Compare Abstr., 1894, i, 208).—When quinaldine and an aqueous solution of tartaric acid are mixed at 60—63°, a crystalline acid tartrate is deposited, which yields an inactive base when decomposed with alkalis. The crystalline salt is not a mixture of *d*- and *l*-hydroquinaldine hydrogen tartrates, but a partially racemic salt.

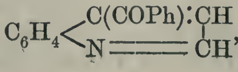
The pure *l*-tetrahydroquinaldine was isolated in the form of the *l*-tartrate by the addition of *l*-tartaric acid to the mother liquor from the *d*-tetrahydroquinaldine *d*-tartrate.

The following data for the salts have been determined:

	M.p.	$D_{18\cdot5}$.	Water of crystallisation.
r-Tetrahydroquinaldine hydrogen tartrate...	72—73°	1·310	1·5H_2O
d-Tetrahydroquinaldine ,, ,, ...	90—91°	1·344	1H_2O
l-Tetrahydroquinaldine ,, ,, ...	62—63°	1·314	1·5H_2O

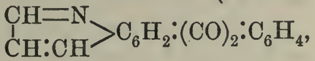
The transition temperature is 59°. J. J. S.

Quinoline Derivatives. III. Phenyl Quinolyl Ketone. Percy Remfry and Herman Decker (*Ber.*, 1908, **41**, 1007—1009. Compare Abstr., 1905, i, 828; 1906, i, 984).—The action of magnesium phenyl bromide on ethyl cinchonate has been studied partly in connexion with the investigations of quinoline derivatives already published, and partly with a view to determining the applicability of carboxylic esters of the pyridine series to Grignard's synthesis. It is found that the action of 1 mol. of magnesium phenyl bromide on 2 mols. of ethyl cinchonate leads to the formation of diphenyl-γ-quinolylcarbinol together with considerable amounts of phenyl γ-quinolyl ketone, but that only traces of the ketone are obtained when 3 mols. of the organo-magnesium compound are added to 1 mol. of the ester.

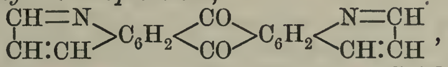
Phenyl γ-quinolyl ketone,  $C_6H_4{<}\begin{matrix}C(COPh){:}CH \\ N{=\!=\!=\!=}CH\end{matrix}$, separates from alcohol in crystalline aggregates, m. p. 294°, and is soluble in mineral acids.

Diphenyl-γ-quinolylcarbinol, $C_9H_6N\cdot CPh_2\cdot OH$, separates from alcohol in small, white crystals, m. p. 247·5°, is soluble in dilute mineral acids, and gives with concentrated sulphuric acid a red coloration which disappears on dilution with water. The *hydrochloride*, yellow crystals, m. p. 223°; the carbinol forms two crystalline *picrates*, the more soluble of which has m. p. 142—144°, whilst the other decomposes at high temperatures. The *methiodide* forms yellow crystals, becoming reddish-brown when dried, m. p. 159°, and gives with sodium carbonate in aqueous solution a white *precipitate*, which becomes violet on exposure to air, can be extracted by ether, and, on evaporation of the ethereal solution, is obtained as a violet residue, m. p. 234°. G. Y.

Preparation of Quinoline Derivatives of the Anthraquinone Series. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 189234).

—*Anthraquinonyl-1-quinoline*,  $\begin{array}{l}CH{=}N\\ |\\ CH{:}CH\end{array}{>}C_6H_2{:}(CO)_2{:}C_6H_4$, yellow crystals, m. p. 169°, is obtained by condensing 1-aminoanthraquinone and glycerol in the presence of concentrated sulphuric acid and nitrobenzenesulphonic acid.

Anthraquinonyl-1 : 5-*diquinoline*,



$$\begin{array}{l}CH{=}N\\ |\\ CH{:}CH\end{array}{>}C_6H_2{<}\begin{array}{c}CO\\ CO\end{array}{>}C_6H_2{<}\begin{array}{l}N{=}CH\\ \quad\ |\\ CH{:}CH\end{array},$$

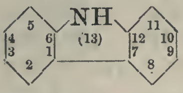
is an almost colourless base, m. p. 342°; the *nitrate*, $C_{20}H_{10}H_2O_2,2HNO_3$, is produced in a similar manner from 1 : 5-diaminoanthraquinone. G. T. M.

Derivatives of Tetra- and Hexa-hydrocarbazoles and a New Synthesis of Carbazole. Walther Borsche [with A. Witte and W. Bothe] (*Annalen*, 1908, 359, 49—80).

—It was shown by Dreschel (Abstr., 1888, 1276) that, when heated with dilute mineral acids, the phenylhydrazone of *cyclo*hexanone yields only small amounts of phenylhydrazine and *cyclo*hexanone, undergoing for the most part a reaction, analogous to Fischer's synthesis of indole from the phenylhydrazones of aldehydes and ketones, in which it loses ammonia and forms tetrahydrocarbazole (compare Baeyer, Abstr., 1894, i, 174). The present authors undertook the study of this little known reaction because it has become of importance in consequence of the ease with which *cyclo*ketones may now be obtained, and, on the other hand, of the increased interest attached to the hydrocarbazoles in connexion with their possible relation to the alkaloids of the strychnine series. The results obtained show that substituting groups in the meta- or para-position in the benzene nucleus of the phenylhydrazine do not, at least markedly, affect the reaction, but that tetracarbazoles are formed only from phenylhydrazones of simple saturated *cyclo*ketones, such as *cyclo*hexanone, *d*-1-methyl-3-*cyclo*hexanone, and *l*-menthone, and not from those of substances such as 1 : 3-dimethyl-Δ^6-*cyclo*hexene-5-one, pulegone, *d*-carvone, and *d*-camphor.

The tetracarbazoles are readily reduced by tin and hydrochloric acid, forming hexahydrocarbazoles (compare Graebe and Glaser, this Journ., 1872, 302), and, in so far as they are volatile, are converted into carbazoles by distillation over finely-divided lead oxide, which must be heated, but not too highly.

The annexed scheme has been adopted in the first part of this paper for the numbering of the positions in carbazole, as the usual method is insufficient for the naming of the new compounds now described.



The hydrazones were for the most part not purified, but heated in the crude state with dilute sulphuric acid on the water-bath.

The action of bromine on tetracarbazole in glacial acetic acid solution leads to the formation of a *hexabromo*-derivative, $C_{12}H_7NBr_6$ or $C_{12}H_8NBr_6$, obtained as a yellow, crystalline powder, unchanged at 300° or on prolonged heating with alcoholic potassium hydroxide or digestion with zinc dust and alcoholic hydrochloric acid, together with a more soluble *tetrabromo*-compound, $C_{12}H_5NBr_4$, m. p. 230°.

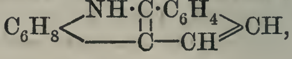
4-*Methyl*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, $C_{13}H_{15}N$, from phenylhydrazine and 1-methyl-3-*cyclo*hexanone, separates from alcohol in crystals, m. p. 94°; the *picrate*, $C_{19}H_{18}O_7N_4$, brownish-red leaflets, m. p. 155°.

9-*Methyl*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, $C_{13}H_{15}N$, from *p*-tolylhydrazine and *cyclo*hexanone, crystallises from light petroleum in white needles, m. p. 141—142°.

4 : 9-*Dimethyl*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, $C_{14}H_{17}N$, from *p*-tolylhydrazine and 1-methyl-3-*cyclo*hexanone, separates from methyl alcohol in transparent plates, m. p. 146°; the *picrate*, dark red leaflets, m. p. 129°.

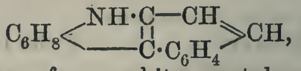
The *phenylhydrazone*, from menthone and phenylhydrazine, forms unstable needles, m. p. 53°, and yields 2-*methyl*-5-iso*propyl*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, $C_{16}H_{21}N$, which crystallises from dilute methyl alcohol in transparent prisms, m. p. 114·5°, b. p. about 150—200°/15 mm.

The *α-naphthylhydrazone* of *cyclo*hexanone, colourless needles, yields $\Delta^{1(6)}$-*tetrahydrobenzo-α-naphthindole*,



$C_6H_8<\begin{array}{l}NH\cdot C\cdot C_6H_4\\ \qquad \| \\ \text{———}C\text{—}CH\end{array}>CH$, white needles, m. p. 139—140°.

$\Delta^{1(6)}$-*Tetrahydrobenzo-β-naphthindole*,



$C_6H_8<\begin{array}{l}NH\cdot C\text{—}CH\\ \qquad \| \\ \text{———}C\cdot C_6H_4\end{array}>CH$, from β-naphthylhydrazine and *cyclo*hexanone, forms white crystals, m. p. 152°.

9-*Methoxy*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, $C_{13}H_{15}ON$, from *p*-methoxyphenylhydrazine and *cyclo*hexanone, crystallises in colourless needles, m. p. 94—95°. The 9-*ethoxy*-compound, $C_{14}H_{17}ON$, prepared in the same manner from *p*-ethoxyphenylhydrazine, forms colourless needles, m. p. 87—88°.

11-*Chloro*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, colourless prisms, m. p. 55—56°, 9-*chloro*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, $C_{12}H_{12}NCl$, needles, m. p. 54—55°, and 9-*bromo*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, colourless plates, m. p. 153°, are prepared from *cyclo*hexanone and *o*-chloro-, *p*-chloro-, and *p*-bromophenylhydrazines respectively.

cyclo*Hexanone*-p-*nitrophenylhydrazone*, $C_{12}H_{15}O_2N_3$, forms yellow needles, m. p. 146—147°. 9-*Nitro*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, $C_{12}H_{12}O_2N_2$, brownish-red crystals, m. p. 174°.

cyclo*Hexanone*-o-*nitrophenylhydrazone*, golden-brown needles, m. p. 74°. 11-*Nitro*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, yellowish-brown leaflets, m. p. 148—149°.

cyclo*Hexanone*-m-*nitrophenylhydrazone*, red needles, m. p. 102—103°. 10-*Nitro*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, red crystals, m. p. 151—152°.

1-*Methyl*-3-cyclo*hexanone*-m-*nitrophenylhydrazone*, $C_{13}H_{17}O_2N_3$, separates from alcohol in crystals, m. p. 90°, and is unstable. 10-*Nitro*-4-*methyl*-$\Delta^{1(6)}$-*tetrahydrocarbazole*, $C_{13}H_{14}O_2N_2$, forms reddish-brown crystals, m. p. 147—148°.

The m-*nitrophenylhydrazones* of 1 : 3-dimethyl-Δ^6-hexene-5-one, red prisms, m. p. 140°, and *d*-carvone, orange-red needles, m. p. 105—106°, and the p-*nitrophenylhydrazone* of *d*-carvone, reddish-brown needles, m. p. 174—175°, are described. Pulegone and *m*-nitrophenylhydrazine form a viscid *condensation product*.

4-*Methylhexahydrocarbazole*, prepared by reduction of the tetrahydrocarbazole with tin and alcoholic hydrochloric acid, crystallises in colourless prisms, m. p. 111°; the *nitroso*-derivative, $C_{13}H_{16}N\cdot NO$, needles, m. p. 62°; the *carbamyl* derivative, $C_{13}H_{16}N\cdot CO\cdot NH_2$, colourless crystals, m. p. 153—154°; the *benzoyl* derivative, $C_{13}H_{16}NBz$, colourless prisms, m. p. 89°.

2-*Methyl*-5-iso*propylhexahydrocarbazole*, $C_{16}H_{13}N$, obtained by reduction of the tetrahydrocarbazole, crystallises in white needles, m. p. 71°; the *nitroso*-derivative, $C_{16}H_{22}ON_2$, yellow prisms, m. p. 140—141°; the *carbamyl* derivative, $C_{16}H_{22}N\cdot CO\cdot NH_2$, colourless needles, m. p. 87—88°.

Carbazole is formed when tetrahydrocarbazole or 9-chloro- or 11-chloro-tetrahydrocarbazole is distilled over lead oxide. The following new substituted carbazoles have been prepared in the same manner from their tetrahydro-compounds. The positions occupied by the substituting groups are numbered in the usual manner.

2-*Methylcarbazole*, $C_{13}H_{11}N$, from 4-methyl-$\Delta^{1(6)}$-tetrahydrocarbazole, crystallises in colourless leaflets, m. p. 259°; the *picrate*, red needles, m. p. 167°. This methylcarbazole is formed also from 6-nitro-3-acetylaminotoluene by conversion of this successively into 4-nitro-*m*-toluidine, 4-*nitro*-3-*anilinotoluene*, and 1-*phenyl*-6-*methylbenzotriazole*, $N\Big\langle\begin{matrix}NPh\\ N\text{---}\end{matrix}\Big\rangle C_6H_3Me$, which on distillation yields the 2-methylcarbazole.

2 : 6-*Dimethylcarbazole* is obtained as a white, crystalline powder, m. p. 208—209°; the *picrate*, light red needles, m. p. 153°.

1 : 3 : 7-Trimethylcarbazole, $C_{15}H_{15}N$, crystallises in white leaflets, m. p. 119°; the *picrate*, m. p. 177°.

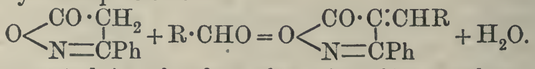
1 : 3 : 4 : 7-*Tetramethylcarbazole*, $C_{16}H_{17}N$, prepared from ψ-cumylhydrazine and *d*-1-methyl-3-*cyclo*hexanone by way of the tetrahydrocarbazole, crystallises in nacreous leaflets, m. p. 153°; the *picrate*, dark red needles, m. p. 146—147°.

4-*Methyl*-1-iso*propylcarbazole*, $C_{16}H_{17}N$, is obtained as a colourless oil, solidifying to a mass of leaflets, m. p. 86°; the *picrate*, light red needles, m. p. 152°.

3-*Methoxycarbazole*, $C_{13}H_{11}ON$, crystallises in colourless needles, m. p. 138—139°; the *picrate*, m. p. 143°. G. Y.

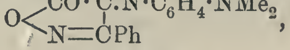
Some Derivatives of Phenyl*iso*oxazolone. André Wahl and André Meyer (*Compt. rend.*, 1908, **146**, 638—640).—Schiff and his pupils have shown (Abstr., 1896, i, 83; 1897, i, 444, 493) that hydroxylamine hydrochloride and an aldehyde condense with ethyl acetoacetate in the presence of aniline, producing solid substances which are formed by the condensation of the aldehyde with the methyl*iso*oxazolone first formed. The authors find that phenyl*iso*oxazolone undergoes a similar reaction. Phenyl*iso*oxazolone, which is best prepared separately, condenses with most aromatic aldehydes on boiling in alcoholic solutions, and in the other cases piperidine is effective as a condensing agent. *Phenylbenzylidene*isoo*xazolone*, $C_3O_2NPh\colon CHPh$, forms bright yellow, shining spangles, m. p. 191° (decomp.).

*Phenylcinnamylidene*isoo*xazolone* crystallises from acetic acid in orange leaflets, m. p. 160° (decomp.). *Phenylfurylidene*isoo*xazolone* forms brown tablets, m. p. 132—133° (decomp.). *Phenyl*-p-*dimethylaminobenzylidene*isoo*xazolone*, $C_3O_2NPh\colon CH\cdot C_6H_4\cdot NMe_2$, crystallises in brick-red shining spangles, m. p. 184°; it has a slight affinity for wool and cotton mordanted with tannin. The derivatives, *phenyl*-o-*hydroxybenzylidene*isoo*xazolone*, yellow needles, m. p. 187°, *phenyl*-p-*hydroxybenzylidene*isoo*xazolone*, yellow needles, m. p. 206—207°, *phenyl-4-hydroxy-3-methoxybenzylidene*isoo*xazolone*, golden-yellow needles, m. p. 213°, and *phenyl-β-hydroxynaphthylidene*isoo*xazolone*, m. p. 223°, which dissolve in alkalis to orange-red solutions, could not be examined for their tinctorial power, since their solutions lose their colour through hydrolysis. The readiness with which phenyl*iso*oxazolone condenses with aromatic aldehydes indicates that it probably contains a methylene group, and that the above reaction should be represented by the equation:



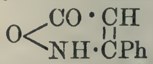
$$\mathrm{O}\left<\begin{matrix}\mathrm{CO\cdot CH_2}\\ \mathrm{N{=}CPh}\end{matrix}\right. + \mathrm{R\cdot CHO} = \mathrm{O}\left<\begin{matrix}\mathrm{CO\cdot C\colon CHR}\\ \mathrm{N{=}CPh}\end{matrix}\right. + \mathrm{H_2O}.$$

This is supported by the fact that phenyl*iso*oxazolone condenses with nitrosodimethylaniline (Sachs, Abstr., 1900, i, 362; 1901, i, 229), giving *phenyl-4-dimethylaminophenylimino*isoo*xazolone*,



$$\mathrm{O}\left<\begin{matrix}\mathrm{CO\cdot C\colon N\cdot C_6H_4\cdot NMe_2}\\ \mathrm{N{=}CPh}\end{matrix}\right.,$$

violet-black needles, m. p. 184° (decomp.).

Relying on its formation by the action of hydroxylamine on ethyl ethoxycinnamate or on phenylpropiolamide, Moureu and Lazennec (Abstr., 1907, i, 716) have proposed the formula  $\mathrm{O}\left<\begin{matrix}\mathrm{CO\cdot CH}\\ \mathrm{NH\cdot CPh}\end{matrix}\right.$ for phenyl*iso*oxazolone. The present work and the preparation by Rabe (Abstr., 1897, i, 568) of two isomeric benzoyl derivatives of phenyl*iso*oxazolone indicate that the latter substance also reacts in the tautomeric methylene form. E. H.

Coloured Salts of Schiff's Bases. Colour as Related to Chemical Constitution. Forris J. Moore and R. D. Gale (*J. Amer. Chem. Soc.*, 1908, **30**, 394—404).—In studying the compound, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NMe_2$, obtained by the condensation of *p*-aminodimethylaniline with piperonal, it was observed that, on treating it with hydrogen chloride, a deep blood-red *hydrochloride* was formed at first and was afterwards converted into a bright lemon-yellow *dihydrochloride.*

It has now been found that *p*-benzylideneaminodimethylaniline (Calm, Abstr., 1885, 387) and the corresponding cinnamylidene, salicylidene, and anisylidene derivatives (Nuth, Abstr., 1885, 784) behave in a similar manner, except that the last-mentioned compound absorbs nearly 3 mols. of hydrogen chloride instead of 2. The *mono-* and *di-hydrochlorides* of these bases are described, and their possible constitution is discussed.

Piperonylidene-p-*toluidine,* m. p. 98°, forms cream-coloured prisms. *Piperonylidene*-p-*chloroaniline* has m. p. 78°. *Ethyl piperonylidene*-p-*aminobenzoate* has m. p. 109°. Piperonal condenses with *m*-nitroaniline and *p*-bromoaniline with formation of *substances* of m. p. 119° and 109° respectively. All these compounds and piperonylideneaniline form only *monohydrochlorides* which are of a yellow colour.

On treating piperonal with *p*-phenylenediamine and with benzidine, *compounds,* m. p. 216° and 241° respectively, are obtained, which are formed by the condensation of 1 mol. of the diamine with 2 mols. of piperonal; these substances form yellow scales with a bronze lustre.

E. G.

Substitution Products of *p*-Diaminodiphenylmethane and of *p*-Diaminodiphenyl. Theodor Neumüller (*J. pr. Chem.*, 1908, [ii], 77, 353—363).—*p*-Diaminodiphenylmethane and its 3 : 3′-dinitro-derivative readily condense with monochloroacetic acid in the presence of sodium acetate, yielding diglycine derivatives. 4 : 4′-*Diphenylmethanediglycine*, $CH_2(C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO_2H)_2$, separates from water or dilute alcohol as a flocculent, crystalline mass, m. p. 175°. 3 : 3′-*Dinitro* - 4 : 4′ - *diphenylmethane diglycine,*

$$CH_2[C_6H_3(NO_2){\cdot}NH{\cdot}CH_2{\cdot}CO_2H]_2,$$

crystallises in lemon-yellow needles, m. p. 164° (decomp.).

3-*Nitro*-4′-*aminodiphenyl*-4-*oxamic acid,*

$$NH_2{\cdot}C_6H_4{\cdot}C_6H_3(NO_2){\cdot}NH{\cdot}CO{\cdot}CO_2H,$$

is readily formed when 4′-aminodiphenyl-4-oxamic acid (D.R.-P. 95060) is nitrated at $-5°$ to $-10°$ with the theoretical amount of potassium nitrate dissolved in concentrated sulphuric acid. It crystallises from alcohol in small, chrome-red aggregates, which melt above 250°. Its *acetyl* derivative, $C_{16}H_{18}O_6N_3$, forms orange-red crystals, which also melt above 250°. The position of the nitro-group in the nitrated oxamic acid follows from the fact that on hydrolysis it yields *o*-nitrobenzidine, and on reduction yields a diamine which, with nitrous acid, gives a diazonium salt and not an azimino-compound, as would be expected if the two amino-groups were in the ortho-positions.

4′-*Acetylaminodiphenyl*-4-*oxamic acid,*

$$NHAc{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CO_2H,$$

crystallises from dilute acetic acid in colourless needles, m. p. above 250°. The *calcium* salt, $C_{32}H_{26}O_8N_4Ca$, crystallises from dilute alcohol in slender needles. When nitrated, the acid yields 3′-*nitro*-4′-*acetyl*-

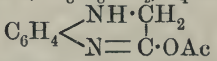
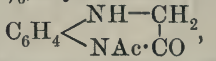
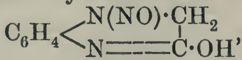
aminodiphenyl-4-*oxamic acid*, $NHAc\cdot C_6H_3(NO_2)\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2H$, which separates from water as a pale orange-red, crystalline mass, m. p. 155°. When boiled with concentrated ammonia, it yields 3′-*nitro*-4′-*aminodiphenyl*-4-*oxamic acid*, in the form of slender needles, m. p. 206°. The fact that the nitro- and acetylamino-groups are in ortho-positions with respect to one another, follows from the readiness with which the acetyl group is eliminated. J. J. S.

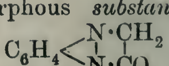
Preparation of 5:5-Dialkylbarbituric Acids from the Corresponding Dialkylmalonylguanidines. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 189076).—The 5:5-dialkylbarbituric acids are obtained in good yield (90—100%) by treating with nitrous acid the dialkylmalonylguanidines produced by condensing the ethyl dialkylmalonates with guanidine, or by condensing the ethyl alkylmalonates with guanidine and alkylating the intermediate product. G. T. M.

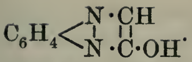
Antipyrine Phosphate and Arsenate. P. AUBOUY (*Bull. Soc. chim.*, 1908, [iv], 3, 388—390).—These two salts have been prepared in extension of previous work on the preparation of the salts of pyramidone with mineral acids (Abstr., 1906, i, 989). Both were obtained by the addition of the respective acids to antipyrine dissolved in alcohol.

Antipyrine phosphate, $[C_{11}H_{12}ON_2]_2,H_3PO_4$, m. p. 158—160°, forms colourless crystals, and is soluble in water, or alcohol, and insoluble in ether. *Antipyrine arsenate*, $[C_{11}H_{12}ON_2]_2,H_3AsO_4$, has m. p. 146—148°, and otherwise resembles the phosphate.

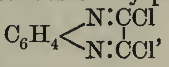
Aqueous solutions of either salt are acid to test paper, and the colour reactions of such solutions with various reagents are recorded. T. A. H.

3-Hydroxy-1:2-dihydroquinoxaline and its Derivatives. SIGMUND MOTYLEWSKI (*Ber.*, 1908, 41, 800—805).—3-Hydroxy-1:2-dihydroquinoxaline, although not formed by the action of *o*-phenylenediamine on ethyl chloroacetate, may nevertheless be prepared by the condensation of *o*-phenylenediamine with chloroacetic acid; it crystallises from water in slender, colourless needles, m. p. 96—97°, containing 1 mol. H_2O; the anhydrous substance has m. p. 132—133°; the *ferrocyanide*, $C_8H_8ON_2,H_4Fe(CN)_6$, crystallises in silvery leaflets. The *acetate*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{NH\cdot CH_2}{N{=}C\cdot OAc}$ or  $C_6H_4{<}\genfrac{}{}{0pt}{}{NH{-}CH_2}{NAc\cdot CO}$, crystallises in colourless needles, m. p. 166°; the *benzoate*, $C_8H_7N_2\cdot OBz$, crystallises in microscopic, white needles, m. p. 210—211°. The parent substance is converted by nitrous acid into 1-*nitroso*-3-*hydroxy*-1:2-*dihydroquinoxaline*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{N(NO)\cdot CH_2}{N{=}C\cdot OH}$, crystallising in yellow, prismatic needles; it melts and partly decomposes at 164°, forming a white mass which becomes transparent at 210°.

Hydrated 3-hydroxy-1:2-dihydroquinoxaline when heated at 125° loses its water of crystallisation together with 2 atoms of hydrogen, being converted into a yellow, amorphous *substance*, m. p. 264° (decomp.); it probably has the formula  $C_6H_4{<}\genfrac{}{}{0pt}{}{N\cdot CH_2}{N\cdot CO}$ or


$C_6H_4<\begin{matrix}N\cdot CH\\ N\cdot C\cdot OH\end{matrix}$. A *substance*, $C_8H_6ON_2$, isomeric with the latter compound, is obtained by the oxidation of 3-hydroxy-1:2-dihydroquinoxaline with potassium permanganate; it crystallises in colourless needles, m. p. 269°, and forms a white, amorphous *silver* salt,

$$C_{16}H_{10}O_5N_4Ag_3,$$

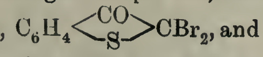
and a green *copper* salt, $C_{16}H_{10}O_4N_4Cu_5$. Oxidation of 3-hydroxy-1:2-dihydroquinoxaline with chromic acid leads to the formation of *o*-phenyleneoxamide, m. p. 410° (compare Seeliger and Meyer, Abstr., 1897, i, 45). The *silver* salt, $(C_{16}H_{10}O_5N_4Ag_4)_2,4\frac{1}{2}H_2O$, and *copper* salt, $C_{16}H_{10}O_7N_4Cu_4$, were prepared. The substance $C_8H_6ON_2$, obtained by the oxidation with potassium permanganate, and *o*-phenyleneoxamide are converted by phosphorus pentachloride into 2:3-*dichloroquinoxaline*,

$C_6H_4<\begin{matrix}N:CCl\\ N:CCl\end{matrix}$, crystallising in colourless needles, m. p. 149—150°. W. H. G.

Preparation of Indoxyl and its Homologues and Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 188436).—The acylarylglycines when condensed with aluminium halides give rise to indoxyl derivatives.

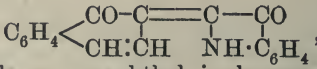
Acetylphenylglycine, its potassium salt, or its ethyl ester when heated with aluminium chloride either in a vacuum or in a current of inert gas at 220—250° furnishes indoxyl, which is isolated in the form of indigotin. Acetyltolylglycine gives rise to the methyl homologue of indigotin. G. T. M.

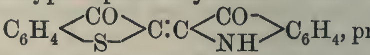
Preparation of Indoxyl and its Homologues. LEON LILIENFELD (D.R.-P. 189021).—It is found that the yield of indoxyl or indigotin obtained by heating phenylglycine with alkali hydroxides in presence of an alkali metal is greatly increased by carrying out this operation under reduced pressure.

The potassium salt of phenylglycine, potassium or sodium hydroxide, and sodium when heated in a good vacuum at 200—250° furnish 80—90% of indigotin. G. T. M.

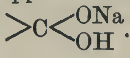
Indigoid Dyes. PAUL FRIEDLÄNDER (*Ber.*, 1908, 41, 772—777. Compare Abstr., 1907, i, 334).—The author applies the term "indigoid" to dyes which are related to indigotin in that the imino-groups of the latter are substituted by a sulphur or other bivalent atom or group. In continuation of the investigation of thioindigotin, now termed bisthionaphthenindigotin in conformity with Jacobson's system of nomenclature (Abstr., 1906, i, 378), it has been found that asymmetric, as well as symmetric, indigoid dyes can be prepared by condensation of substances such as indoxyl, thioindoxyl, 1:3-diketohydrindene, α- and β-naphthols, and the more reactive phenols of the benzene series, which contain the grouping ·CO·CH₂· or ·C(OH):CH·, with cyclic α-diketones, such as isatin, α-keto-halogen compounds, such as isatin chloride or dibromo-oxythionaphthen,

$C_6H_4<\begin{matrix}CO\\ S\end{matrix}>CBr_2$, and reactive anilinoketones and alkyloxyketones, such as the α-anilide and α-methyl ether of isatin. The

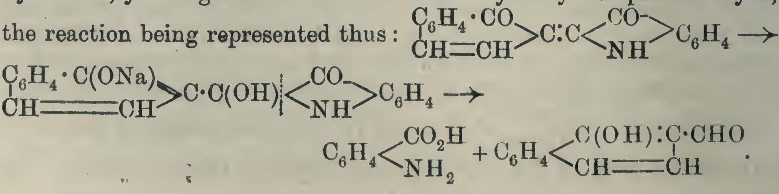
products are all coloured orange-red to greenish-blue. They vary in stability and in their behaviour towards alkalis with the nature of the two cyclic nuclei of which they are composed, but are in general stable towards acids, and on treatment with alkaline reducing agents yield colourless products mostly easily oxidised by the atmospheric oxygen with formation of the original dye. The following two new indigoid dyes are described.

Naphthalene-indole-indigotin, 
$C_6H_4<\begin{array}{l}CO-C=\!=C-CO\\ CH{:}CH\quad NH\cdot C_6H_4\end{array}$, prepared by the action of isatin chloride on α-naphthol in benzene solution, crystallises in copper-coloured prisms or needles, m. p. about 240°, and forms at higher temperatures a reddish-violet vapour which condenses to woolly needles. It is more easily soluble than indigotin, and is sulphonated with difficulty, yielding a *product* which is less stable towards alkalis than is indigo-carmine. When boiled with sodium carbonate solution, the indigotin forms a greenish-yellow, soluble *sodium* compound, readily decomposed by acids, and when boiled with sodium hydroxide dissolves and is rapidly decomposed. The solution obtained on reduction with alkaline hyposulphite is yellow.

2-*Thionaphthen-2-indole-indigotin*, 
$C_6H_4<\begin{array}{c}CO\\ S\end{array}>C{:}C<\begin{array}{c}CO\\ NH\end{array}>C_6H_4$, prepared by heating indoxyl with dibromo-oxythionaphthen in glacial acetic acid solution, crystallises from nitrobenzene in reddish-violet needles, does not melt at 300°, sublimes at higher temperatures, and forms a slightly yellow reduction *product*, which dyes textile fibres bluish-violet. The *sulphonic acid* is blue and becomes yellow on addition of an excess of alkali.

The absorption spectra of thioindigotin and of the two new indigoid dyes are described. G. Y.

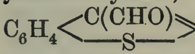
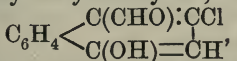
Behaviour of Indigoid Dyes and Indigotin towards Alkalis. PAUL FRIEDLÄNDER (*Ber.*, 1908, 41, 1035—1039. Compare preceding abstract).—Binz has shown (Abstr., 1906, i, 749) that indigotin forms an additive product with sodium hydroxide having the composition $C_{16}H_{10}O_2N_2,NaOH$, in which he supposed the sodium hydroxide to be attached to a carbonyl group, thus: 
$>C<\begin{array}{l}ONa\\ OH\end{array}$. Since indigotin and quinones contain the group $-CO\cdot\overset{|}{C}{:}\overset{|}{C}\cdot CO-$, which on the addition of acetic acid changes into $-C(OH){:}CH\cdot CH(OAc)\cdot CO-$ or
$-C(OH){:}CH\cdot C(OAc){:}C(OH)-$,
the author considers it probable that the sodium hydroxide would combine in a similar manner. This view receives support from the fact that 2-naphthalene-2-indoleindigotin is decomposed by sodium hydroxide, yielding anthranilic acid and 1-hydroxy-2-naphthaldehyde, the reaction being represented thus:



$$\begin{array}{l}C_6H_4\cdot CO\\ CH=CH\end{array}>C{:}C<\begin{array}{c}CO-\\ NH\end{array}>C_6H_4 \rightarrow \begin{array}{l}C_6H_4\cdot C(ONa)\\ CH=\!=\!=CH\end{array}>C\cdot C(OH)\Big|<\begin{array}{c}CO-\\ NH\end{array}>C_6H_4 \rightarrow$$

$$C_6H_4<\begin{array}{l}CO_2H\\ NH_2\end{array} + C_6H_4<\begin{array}{l}C(OH){:}C\cdot CHO\\ CH=\!=\!=CH\end{array}.$$

1-*Hydroxy-2-naphthaldehyde*, $C_{11}H_8O_2$, crystallises in long, pale greenish-yellow needles, m. p. 59°; it is very similar to salicylaldehyde, gives a crystalline *hydrazone*, and when treated with methyl sulphate in alkaline solution yields 1-*methoxy-2-naphthaldehyde*, crystallising in white, compact prisms, m. p. 47°.

2-Hydroxy-1-naphthaldehyde has been obtained by warming 1-naphthalene-2-indoleindigotin with 10% aqueous sodium hydroxide solution. Similarly, 1-*hydroxy-4-methoxy-2-naphthaldehyde*, lemon-yellow crystals, m. p. 100°, and 2-*hydroxy-3-thionaphthenaldehyde*,  $C_6H_4{<}\begin{matrix}C(CHO)\\S\end{matrix}{>}C\cdot OH$, m. p. 130°, have been prepared from 4-methoxy-2-naphthalene-2-indoleindigotin and 3-thionaphthen-2-indoleindigotin respectively. The *p*-quinonoid compounds which are formed together with the indigoid dyes by the condensation of isatin chloride with certain phenols and naphthols are also decomposed by alkali, yielding hydroxy-aldehydes; for example, 2-*chloro-4-hydroxy-1-naphthaldehyde*,  $C_6H_4{<}\begin{matrix}C(CHO){:}CCl\\C(OH){=}CH\end{matrix}$, m. p. about 220° (decomp.), is obtained from the product which results on condensing isatin chloride with 2-chloro-α-naphthol. W. H. G.

Action of Halogens on Aromatic Amines and their Use in the Synthesis of Certain Dyes. Adriano Ostrogovich and T. Silbermann (*Chem. Zentr.*, 1908, i, 266; from *Bul. Soc. Stiinte Bucuresci*, 1907, **16**, 120—126).—Iodine, bromine, and chlorine react with aniline at 140—180° giving dyes of the induline class. If a mixture of aniline hydrochloride and α-naphthylamine is subjected to the action of iodine in presence of aniline, a substance of the nature of a rosinduline is produced. *p*-Toluidine when heated at 140—180° with aniline and iodine gives *p*-rosaniline hydriodide. J. V. E.

Oxidation of Aniline by Halogen Acids. Adriano Ostrogovich and T. Silbermann (*Chem. Zentr.*, 1908, i, 266; from *Bul. Soc. Stiinte Bucuresci*, 1907, **16**, 127—133).—In the presence of mineral acids, chloric, bromic, and iodic acids oxidise aniline to aniline-black. In presence of acetic acid, aniline is scarcely attacked by chloric acid; with bromic acid it yields dianilinoquinoneanil, and with iodic acid, azophenine. When dianilinoquinoneanil is melted with aniline hydrochloride and aniline, a blue induline dye is obtained; by using *p*-phenylenediamine in place of aniline, a bluish-violet induline dye is obtained; *o*-aminophenol, *p*-aminophenol, and *p*-phenylenediamine react in this respect like aniline. J. V. E.

Explanation of the Formation of Induline. Adriano Ostrogovich and T. Silbermann (*Chem. Zentr.*, 1908, i, 266—267; from *Bul. Soc. Stiinte Bucuresci*, 1907, **16**, 133—141).—When aniline-black is heated at 180° with excess of an aniline salt, induline is quantitatively formed; from this and other observations, the author concludes that aniline-black is an intermediate product in the oxidation of aniline to induline. J. V. E.

Glycine as a Product of Uricolysis. Lyman B. Stookey (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xxx.; *J. Biol. Chem.*, 4).—Although

in vitro uric acid may be readily degraded to glycine, it is unsettled whether glycine is an intermediary product in uricolysis. Minced liver and kidney were incubated with uric acid and benzoic acid; the greater portion of the uric acid was destroyed, but there was no corresponding increase of hippuric acid; hence glycine was not formed.
W. D. H.

Azoxy-compounds. Th. Rotarski (*Ber.*, 1908, 41, 865—866).—The liquid, crystalline modifications of azoxybenzene, *m*-azoxytoluene, *m*-azoxyanisole, and *p*-azoxyphenetole are reduced in acid solution to amino-compounds and in alkaline solution or by distillation with iron to azo-compounds, but differ from the solid forms in the following respects: (1) They respond to Liebermann's nitroso-reaction. (2) The solution in boiling glacial acetic acid is coloured red by hydrochloric acid, D 1·19. (3) The yellow colour is unchanged by sunlight. (4) Sulphuric acid does not convert them into hydroxyazo-compounds. (5) The additive compound with bromine, formed in chloroform solution, loses hydrogen bromide when melted.

The temperature at which the turbid liquid crystals become clear is unchanged by crystallisation or distillation.

m-*Azoxyanisole*, m. p. 51°, obtained from *m*-nitroanisole and sodium methoxide, becomes red on exposure to light, and by distillation with iron filings yields m-*azoanisole*, m. p. 73—74°.
C. S.

Constitution of the Acetylated Condensation Products from Benzeneazo-α-naphthol and Tetramethyldiaminobenzhydrol. Richard Möhlau (*Ber.*, 1908, 41, 989—990. Compare Möhlau and Kegel, Abstr., 1900, i, 56).—The author confirms Auwers and Eisenlohr's statement (this vol,, i, 229) that, when the acetylated condensation product is reduced, acetanilide is not formed, but aniline; hence the argument for the hydrazone constitution for the condensation product is no longer valid.
J. J. S.

Chloroamine Reaction of the Proteins. Charles F. Cross, Edward J. Bevan, and John F. Briggs (*J. Soc. Chem. Ind.*, 1908, 27, 6, 260).—The reaction of chlorine and hypochlorites on nitrogenous colloids to form chloroamine derivatives is shown to take place in constant and characteristic quantitative proportions, the derivatives being formed without destructive actions. The bearing of the fixation of "active" chloroamine chlorine on bleaching processes and the application of chloroamine reactions to histological investigations are dealt with in detail.
J. V. E.

Hydrolysis of Different Proteins in Pepsin-Acid Solutions. William N. Berg (*Proc. Amer. Soc. Biol. Chem.*, 1907—8, xlv.; *J. Biol. Chem.*, 4).—Various proteins and various acids of strength equivalent to 0·2% hydrochloric acid were employed. Edestin digests most rapidly, then follow in the order given, alkali-albumin, acid-albumin, fibrin, egg-albumin, nucleo-protein, and elastin. The order of the acids in efficiency is hydrochloric, nitric, oxalic, phosphoric, sulphuric, tartaric, lactic, citric, acetic, and boric.
W. D. H.

The Preparation of *iso*Leucine from the Hydrolysis Products of Proteins. Phœbus A. Levene and Walter A. Jacobs (*Biochem. Zeitsch.*, 1908, 9, 231—232).—The principal difficulty which has existed hitherto in the preparation of pure leucine and its isomeride consists in the separation of valine from the leucines. This can be best accomplished by precipitation of the latter substances by normal lead acetate and ammonia. The leucines were prepared from casein in the following way. The casein was hydrolysed with 33% sulphuric acid, and the latter separated by barium hydroxide. On evaporation of the filtrate from barium sulphate, a mixture of tyrosine and leucine separated. On addition of bromine, the bromo-compound of the former substance was obtained, and could be dissolved out with amyl alcohol. On further evaporation of the liquid after this treatment, the leucine-valine mixture separated. This was redissolved, and the crude leucine precipitated by lead acetate and ammonia. On decomposing the lead precipitate with hydrogen sulphide, a mixture of leucine and *iso*leucine was obtained, from which the constituents could be readily separated by treatment of the copper salts with methyl alcohol. S. B. S.

Influence of Electrolytes on the Coagulation-temperature of Egg-albumin. Wolfgang Ostwald (*Chem. Zentr.*, 1908, i, 89; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 108—113).—By using the figures of Bonamartini and Pauli (Abstr., 1907, i, 802), the dependence of the coagulation-temperature of various solutions of egg-albumin on the concentration of an added salt, such as NaCl or NH_4Cl, is represented with great accuracy by the equation: $1/t = Kc^m$, where t = coagulation-temperature, c = salt concentration, and K and m = constants. By altering the coagulation-temperature to 16° and a salt concentration from 1% to 20%, m only varies between 0·08 and 0·21. The similarity of the above equation to the general adsorption equation apparently shows a connexion between the temperature of coagulation of egg-albumin in presence of electrolytes and adsorption phenomena in solution. The attempt of Freundlich (Abstr., 1907, ii, 939) to connect the phenomena of coagulation with ion adsorption is criticised. J. V. E.

Adsorption of Acids by Casein. Lucius L. van Slyke and Donald D. van Slyke (*J. Biol. Chem.*, 1908, 4, 259—266).—In spite of criticisms by T. B. Robertson (this vol., ii, 89), the authors maintain that the relationship between casein and acids is one of adsorption rather than chemical combination. W. D. H.

Preparation and Some Properties of the Oxyhæmocyanin Crystallised from the Snail. C. Déré (*Compt. rend.*, 1908, 146, 784—786).—When snail's blood is dialysed in a collodion bag in the presence of distilled water, renewed morning and evening, at the temperature of melting snow, it remains perfectly limpid during the first seven days. In the course of the eighth day, the blood becomes cloudy, and soon deposits an abundant precipitate of oxyhæmocyanin, the azure colour of the liquid becoming paler. Microscopic examination of the deposit shows that it consists entirely of crystals in the form of six-pointed stars, which are not birefringent. After sixteen days, the supernatant liquid has become practically colourless, and is not altered by agitation with air. If after seven days the dialysed blood is subjected to the action of a continuous current of 0·1 milliampere at 120 volts, the oxyhæmocyanin is deposited at the anode, whilst the liquid surrounding the cathode becomes colourless, but, on shaking the whole liquid, the crystals of oxyhæmocyanin redissolve to a blue-coloured solution.

Oxyhæmocyanin, after calcination, leaves a small quantity of a black residue, which dissolves in nitric acid and contains copper. It dissolves in water containing a trace of acetic acid. The absorption spectrum given by a layer 3 mm. thick of a solution containing 7·59 grams of oxyhæmocyanin per litre presents a band in the ultraviolet between λ 292·6 and λ 262·8. On increasing the thickness of the layer, a fresh band appears, and at 10 mm. extends from λ 364·0 to λ 328·2. The latter band seems to be characteristic; the most refrangible band is common to all albuminous substances. E. H.

Soluble Silver Compounds of Nucleic Acids and their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 188435).—The silver compound of sodium nucleate from yeast is obtained as a thick paste by adding aqueous silver nitrate to a strong solution of the nucleate in water. A saturated solution of sodium chloride is added until the precipitate has redissolved, when the compound is reprecipitated with alcohol. The product is a yellowish-white powder containing 22% to 23% of silver.

Sodium nucleate from the thymus gland gives a similar derivative, as do also the formaldehyde derivatives of these acids. G. T. M.

Pyrimidine Derivatives in Nucleic Acid. THOMAS B. OSBORNE and FREDERICK W. HEYL (*Amer. J. Physiol.*, 1908, 21, 157—161).—The question has arisen whether or no the pyrimidine derivatives of nucleic acid originate from the purine substances in the presence of carbohydrates. In the present research, the purines were first removed by mild hydrolysis; severe hydrolysis then liberated the pyrimidine compounds. The fact that the mild hydrolysis completely removed the purine, is shown by no ammonia being liberated during the severe hydrolysis, for each molecule of pyrimidine which is formed from the purines involves the production of two molecules of ammonia. The further conclusion is drawn that uracil is not derived from cytosine, for this also involves the production of ammonia. W. D. H.

The Origin of Cytosine, obtained by the Hydrolysis of Nucleic Acids of Animal Origin. PHŒBUS A. LEVENE and JOHN A. MANDEL (*Biochem. Zeitsch.*, 1908, 9, 233—239).—The estimation of cytosine obtained in different stages of partial and also in complete hydrolysis of nucleic acid of spleen was carried out. The results lead to no definite conclusion as to whether the cytosine is of secondary origin or not, that is, whether it is derived from the hydrolysis of purine compounds or directly from the original nucleic acid molecule. S. B. S.

Reducing Action of Animal Fibres. GUSTAV ULRICH [and, in part, THEODOR SCHMIDT] (*Zeitsch. physiol. Chem.*, 1908, **55**, 25—41).—These investigations were carried out with the object of determining the action of wool on the mixture of chromium trioxide and formic acid, as employed in mordanting processes. The direct reducing action of the formic acid on the chromium trioxide appears to be but small. The formic acid acts on the fibres with the production of substances which bring about the reduction of chromium trioxide.

S. B. S.

Behaviour of Gelatin Solutions Towards Naphthols or Mixtures of Naphthols with Formaldehyde. ARTHUR WEINSCHENK (*Chem. Zeit.*, 1908, **32**, 266—267).—A reply to Stiasny's statements concerning the author's observations on the tanning of hides by means of naphthols in the presence of aldehydes. The addition of formaldehyde to a solution obtained by adding β-naphthol dissolved in glycerol to a strong aqueous solution of gelatin, produces a thick, flaky precipitate which is quite insoluble in water, whereas no such precipitate is formed in the absence of β-naphthol. P. H.

Some Oxides as Tanning Material. LÜPPO-CRAMER (*Chem. Zentr.*, 1908, i, 93—94; from *Zeitsch. Chem. Ind. Kolloide*, 1907, **2**, 171—173).—The author found previously (Abstr., 1907, i, 1098) that gelatin absorbs soluble salts without becoming tanned, whereas colloidal silver oxide acts as a typical tanning material. Silver peroxide, prepared from silver nitrate and ammonium persulphate, is now shown to be a far more powerful tanning agent. The silver peroxide compound of gelatin is insoluble in boiling water and unchanged by sodium hydroxide, ammonia, sodium thiosulphate, or dilute sulphuric acid, but is decomposed when warmed with strong acids. Metol-soda developer darkens the yellow colour, partly reduces the peroxide to silver, and does not destroy the tanning. A photographic negative desilverised by ammonium persulphate behaves in a similar manner, and, since a 10% potassium cyanide solution removes the image but does not destroy the tanning, the photobromide remaining in the negative plays no part in the tanning. Silver peroxide itself coagulates concentrated solutions of gum arabic. Mercury and copper oxides tan gelatin, rendering it insoluble. The HgO-gelatin shows unusual hardness, and, like Ag_2O-gelatin, when warmed in water becomes intensely white. CuO-gelatin is green, and by washing out excess of salt the tanning is not destroyed.

In the coagulation of egg-albumin by silver nitrate solution, adsorption compounds of silver oxide with egg-albumin are formed which are not attacked by thiosulphates. In all albumin papers therefore, after fixing and washing, there remains some silver oxide which may cause the paper to become yellow. J. V. E.

Lipoids. SIGMUND FRÄNKEL (*Biochem. Zeitsch.*, 1908, **9**, 44—53). **Part I. Neottine, a Triaminophosphatide.** CARLO BOLAFFIO.—Two substances have been prepared from egg-yolks containing nitrogen and phosphorus, the one with the element in the ratio 8N : 1P, and the other, a triaminophosphatide, designated *neottine.*

The former was prepared by extracting egg-yolks with acetone, filtering, distilling off the acetone, and again extracting the residue left with ether. On distilling off the latter solvent, crystals were deposited, and were separated from the liquid fats by aid of a porous tile. They were only partly soluble in acetone; the solution in this solvent gave a precipitate with cadmium chloride in alcoholic solution, which was soluble in hot benzene and could be recrystallised from boiling 95% alcohol. The cadmium compound thus obtained was crystalline and readily darkened on exposure to air, and was therefore probably an unsaturated compound. It contained 1·84% N and 0·51% P.

The second compound, *neottine*, $C_{84}H_{172}O_{15}N_3P$, was obtained by extracting dried egg-yolks with acetone until a white residue was obtained; this was digested for two hours at 45° with double its weight of 95% alcohol. The filtered extract, on evaporation in a vacuum, gave a white residue, which showed little change on exposure to air; the subsequent alcoholic extract of the residue darkened, however. The substance from the first extract was recrystallised several times from hot alcohol, and a white substance was finally obtained which could be readily powdered; the powder consisted of a fine network of microscopic needles, m. p. 91°. The molecular weight was confirmed cryoscopically. The substance absorbs but a small quantity of iodine, the Hübl number being only 16·2, and is optically inactive. It was found by the Herzig and Mayer method that only one-third of the nitrogen is combined with methyl groups (that is, in the form of choline). On hydrolysis with barium hydroxide, three acids were obtained, presumably cerebronic, stearic, and palmitic acids.

S. B. S.

Synthetic Tryptophan and Some of its Derivatives. ALEXANDER ELLINGER and CLAUDE FLAMAND (*Zeitsch. physiol. Chem.*, 1908, 55, 8—24).—By the reduction of *a-benzoylaminoindolylacrylic acid*, $C_8H_6N\cdot CH\colon C(NHBz)\cdot CO_2H$, with sodium and alcohol, racemic tryptophan has been obtained (Abstr., 1907, i, 737). For identification and comparison with the natural dextrorotatory substance, the *benzenesulphonyltryptophans*, $C_8H_6N\cdot CH_2\cdot CH(NH\cdot SO_2Bz)\cdot CO_2H$, the corresponding *β-naphthalenesulphonyltryptophans*, and the *tryptophannaphthylcarbimides* were prepared. The derivatives from the natural dextrorotatory substance and the racemic synthetical compound had identical melting points (185°, 180°, 158°). The naphthylcarbimide compound is very sensitive to light. The paper gives, in addition, the details of the preparation of the synthetical substance. S. B. S.

Optical Behaviour of Tryptophan. H. FISCHER (*Zeitsch. physiol. Chem.*, 1908, 55, 74—76).—Tryptophan and its hydrochloride are lævorotatory, whilst the sodium salt is dextrorotatory. The rotation in aqueous solutions shows considerable variations, which cannot be accounted for by polymerisation. There is no reason to alter the original designation of Hopkins and Cole of *l*- into *d*-tryptophan.

S. B. S.

Union of Carbon Dioxide with Amphoteric Amino-compounds. III. MAX SIEGFRIED and C. NEUMANN (*Zeitsch. physiol. Chem.*, 1908, **54**, 423—436. Compare Abstr., 1905, ii, 332; 1906, i, 324).—The amount of carbon dioxide absorbed in the formation of carbamic acids from amino-compounds is determined by adding to 0·1—0·5 gram of the substance, dissolved in 50 c.c. of ice-cold water, a few drops of phenolphthalein in lime-water, and then about 10 c.c. of milk of lime, containing 20% of calcium hydroxide. Carbon dioxide is passed in until the indicator is almost decolorised while the solution is gently shaken. The addition of milk of lime and its neutralisation by carbon dioxide is repeated three to four times. The solution of the calcium carbamate is filtered clear and boiled; the calcium carbonate which is thus precipitated is weighed, and the nitrogen in the filtrate is determined by Kjeldahl's method.

A number of amino-acids and other substances have been examined, and the molecular ratio of ammonia to carbon dioxide approximates in nearly all cases rather closely to a whole number (in accordance with the theory). The reaction has been applied fractionally to a gluco-albumose, first obtained by Pick. The purity of the substance is deduced from the constancy of the nitrogen content of the fractions.

G. B.

Union of Carbon Dioxide with Amphoteric Amino-compounds. IV. MAX SIEGFRIED and HANS LIEBERMANN (*Zeitsch. physiol. Chem.*, 1908, **54**, 437—447).—The method described in the preceding abstract has been applied to polypeptides. In the case of glycylglycine, the ratio N/CO_2 is 1·79; this seems to be due to the formation of the *ammonium* salt of glycylglycine-carboxylic acid, m. p. 206° (almost identical with that of the acid itself). Glycylglycine-carboxylic acid does not unite with carbon dioxide in the presence of lime.

For a number of dipeptides, the ratio N/CO_2 was 1·63—1·79; for tripeptides, 2·57; for a tetrapeptide, 3·29; for trypsin-fibrin-peptone-α and -β (Abstr., 1903, i, 782) it was 2·14—2·46. Since these peptones cannot be as simple as di- or tri-peptides, the explanation of the low value (2·14—2·46) is sought in the possible presence of hydroxyl groups in the peptones; small quantities of alcohol, when present in the reaction mixture (for instance, as alcoholic phenolphthalein), lower the ratio very considerably. G. B.

Serum Containing Anti-amylase. C. GESSARD and JULES WOLFF (*Compt. rend.*, 1908, **146**, 414—416).—As was shown by Gessard (*Compt. rend. Soc. Biol.*, 1906, **61**, 425), a serum can be prepared inhibiting the action of malt-extract on starch. In the present experiment, the greatest degree of inhibition is 70%, as determined by the amount of maltose produced. At 50°, the inhibitory effect is only half as great as at 20°. G. B.

Tyrosinase and Racemic Tyrosine. GABRIEL BERTRAND and M. ROSENBLATT (*Compt. rend.*, 1908, **146**, 304—306; *Bull. Soc. chim.*, 1908, [iv], **3**, 394—398).—The oxidation of *d*-tyrosine and of *l*-tyrosine and of *dl*-tyrosine by tyrosinase (from *Russula*) takes place at the same rate. Accordingly, there is only one ferment for both antipodes.

G. B.

The Co-enzyme of Expressed Yeast in Juice. EDUARD BUCHNER and FRITZ KLATTE (*Biochem. Zeitsch.*, 1908, 8, 520—557).—Previous researches have shown that the fermentative activity of yeast is due to two substances, the zymase, which is destroyed by boiling the expressed juice, and a co-enzyme, which is not so destroyed; the latter only can dialyse through parchment, and can also be separated from the former by filtration through a Martin gelatin filter.

Further experiments have been carried out with a view of throwing light on the chemical nature of these substances. Considerable differences were noted in their activity in yeasts of different origin; the juice from Berlin yeast, for example, could be better regenerated by the addition of boiled juice after it had lost its activity, than could that from Munich yeast. This fact may account for some of the discrepancies in the observations of different observers.

This regeneration could be accomplished in some cases as many as six or seven times, and the zymase was still active even after twenty-seven days. These facts indicate that the co-enzyme is much more readily destroyed than the zymase.

Yeast juice, which has become inactive by keeping without sugar, cannot be regenerated; neither can a co-enzyme be prepared from it. It is known that the proteoclastic enzyme contained in yeast can destroy the zymase, and experiments were carried out to determine whether it exerted a similar action on the co-enzyme. It was found that the co-enzyme lost but little of its activity after treatment with trypsin; it is improbable, therefore, that the tryptic enzyme of the yeast is responsible for the destruction; furthermore, on mixing the co-enzyme (boiled yeast juice) with fresh juice without sugar, it rapidly loses its activity. If, however, the juice is six months old, it exerts no destructive action on a co-enzyme, even although it retains its proteoclastic activity. The tryptic enzyme presumably destroys the substance which acts on the co-enzyme. Boiled juice, however, on treatment with lipase from castor-oil seeds rapidly loses its co-enzymic activity, and this fact leads to the supposition that the co-enzyme is of the nature of a phosphoric ester. It was found, in fact, that sodium glycerophosphate has considerable power in regenerating the inactivated zymase.

S. B. S.

The Chemical Changes in Adrenaline produced by Enzymes. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 8, 383—386).—The extract from the ink bag of *Sepia officinalis* has the power of producing a black pigment from adrenaline, which is insoluble in alcohol but partly soluble in alkalis; it is an oxidation product. Other substances from the animal organism, which yield colours, were investigated, but only tryptophan and tyrosine yielded pigments. The action is due to an enzyme, as the boiled extract has no action.

S. B. S.

Organic Chemistry.

Relative Volatility of Certain Groups of Mixed Carbon Compounds. II. Mixed Methylenic Compounds. Louis Henry (*Bull. Acad. roy. Belg.*, 1908, 6—17. Compare this vol., i, 305).—A continuation of the author's discussion of the volatility relations of carbon compounds, dealing with substances of the types CH_2XX' and $CH_3 \cdot CHXX'$. Numerous examples are quoted to show that in some cases the boiling point of a mixed compound is approximately the arithmetic mean of those of the two corresponding simple substances; thus dimethoxymethane, $CH_2(OMe)_2$, has b. p. 42°, and diethoxymethane, $CH_2(OEt)_2$, has b. p. 88°, whereas *methoxyethoxymethane*, $OMe \cdot CH_2 \cdot OEt$, obtained by the action of sodium ethoxide in alcohol on chloromethoxymethane, $CH_2Cl \cdot OMe$, has b. p. 67°. In such cases, it is suggested that the liquids show no molecular association. In other instances, for example, in the group CH_2Cl_2, b. p. 42°, $CH_2(OMe)_2$, b. p. 42°, and $OMe \cdot CH_2Cl$, b. p. 59°, the boiling point of the mixed compound is above the arithmetic mean. A second illustration of this is afforded by the group diphenoxymethane, $CH_2(OPh)_2$, b. p. 298°, which crystallises at $-8°$, dimethoxymethane, b. p. 42°, and the methoxyphenoxymethane, $OMe \cdot CH_2 \cdot OPh$, b. p. 189° (compare Reychler, this vol., i, 159).

Similar illustrations of these two relationships are quoted from ethylidene compounds of the type $CHMe \cdot XX'$. T. A. H.

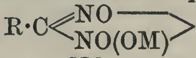
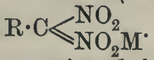
Volatility in the "Methylation" Series of Methyl Derivatives. Louis Henry (*Bull. Acad. roy. Belg.*, 1908, 66—81. Compare this vol., i, 305, and preceding abstract).—A study of the effect of the continued substitution of CH_3- for $H-$ in simple methane derivatives.

Taking the four compounds $MeCl$, CH_2MeCl, $CHMe_2Cl$, CMe_3Cl, the difference in boiling point between each successive pair diminishes regularly by 9°, which is in agreement with the observation that the alkyl haloids are non-associated liquids, since in such a case the substitution of $-CH_3$ for $H-$ involves a simple gravimetric effect, and does not imply any simplification or otherwise in the molecule as a whole.

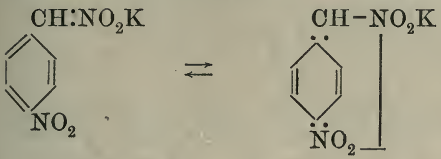
The case is quite different in the series $H \cdot OH$, $CH_3 \cdot OH$, $CH_2Me \cdot OH$, $CHMe_2 \cdot OH$, and $CMe_3 \cdot OH$, where the differences in boiling point between each successive pair are $-34°$, $+12°$, $+4°$, $\pm 0°$ respectively. Here the changes in boiling point are due to two causes operating simultaneously: (*a*) the gradual simplification of a complex associated molecule causing a diminution in boiling point, and (*b*) the increase in molecular weight due to the substitution of $H-$ by $-CH_3$ causing a rise in boiling point. The operation of the same two causes, but especially of the first, is also seen in the series $HO \cdot H$, $MeO \cdot H$,

$Me\cdot O\cdot Me$, where the differences between each successive pair are $-34°$ and $+89°$ respectively, methyl ether being much less associated than either water or methyl alcohol. Mercaptans are less associated than alcohols, and consequently the gradual substitution of methyl in compounds of this series has much the same effect as in the case of the haloids, for example, $Me\cdot SH$, $CH_2Me\cdot SH$, $CHMe_2\cdot SH$, $CMe_3\cdot SH$, where the difference between each successive pair diminishes regularly by 10°. Similar discussions of the corresponding bromides, iodides, ethers, esters, nitrites, cyanides, &c., are given, and each of these groups approximates more or less closely in its behaviour to one of the two types mentioned above. T. A. H.

Spectroscopical Investigation of Isomerisable Nitro-compounds in Ultra-violet. Edgar P. Hedley (*Ber.*, 1908, **41**, 1195—1203).—Nitromethane, dinitromethane, trinitromethane, bromodinitromethane, dinitroethane, phenyldinitromethane, *o*-, *m*-, and *p*-nitrophenylnitromethane, and their alkali salts have been investigated in the ultra-violet by the method described by Hartley (Trans., 1885, **47**, 685).

The absorption curves of the colourless solutions of the mononitro-compounds in indifferent solvents are different from those of the colourless, alkaline solutions of the same compound, from which it follows, as has been shown by Ley and Hantzsch (Abstr., 1906, i, 790), that the former solutions contain the true nitro-compound, $R\cdot CH_2\cdot NO_2$, whereas the latter contain the salts of the isomeric *aci*-nitro-compound, $R\cdot CH{:}NO_2M$. Similarly, the absorption curves of the colourless solutions of dinitromethane, bromodinitromethane, and nitroform in ether, and of phenyldinitromethane in chloroform, are totally different from those of the yellow aqueous or alcoholic solutions of these compounds and of dinitroethane, which are very similar to the absorption curves of the solutions of the alkali salts of these compounds. The latter curves are analogous to those obtained by Baly with the nitroanilines (Trans., 1906, **89**, 514), and are totally different from those shown by the *aci*-mononitro-salts, $R\cdot CH\cdot NO_2M$. It is therefore evident that, as has been demonstrated by Hantzsch (Abstr., 1907, i, 500), the coloured solutions of the dinitro-paraffins contain a highly isomerised form with a quinonoid grouping, which may be represented thus :  $R\cdot C\Big<\begin{array}{l}NO\text{———}\\NO(OM)\end{array}\Big>O$, and do not contain the simple isomeric *aci*-form,  $R\cdot C\Big<\begin{array}{l}NO_2\\NO_2M\end{array}$. The intensity of these solutions is proportional to the quantity of this form present in the solution; thus solutions of the alkali salts show a deeper band than the solutions of the substances in water, which in turn persists longer than that of a solution containing hydrochloric acid.

The colourless solutions of the nitrophenylnitromethanes in indifferent solvents do not show any absorption bands; the solutions of the alkali salts, however, show an absorption similar to that of dinitromethane salts, together with the characteristic benzene bands in the ultra-violet. It is probable that the colourless solutions contain the true dinitro-compound, $NO_2·C_6H_4·CH_2·NO_2$, whereas the solutions of the salts contain the benzenoid and quinonoid salts in a state of equilibrium. It is also seen from the curves that the intensity of the benzene band is greatest in the case of the meta-salts, and least with the para-salts, whilst the converse applies to the quinonoid band.



The colour of these similarly constituted compounds deepens with an increase in the molecular weight. W. H. G.

Densities of Solutions of Trimethylcarbinol and Phenol. Emanuale Paternò and Aldo Mieli (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 396—400).—It has been found previously (compare Paternò and Ampola, Abstr., 1897, ii, 476) that the equilibrium curve for mixtures of trimethylcarbinol and phenol exhibits two maxima, which should correspond with definite chemical compounds, and three minima, corresponding with three eutectic mixtures. The density-composition curves for mixtures of these two compounds at 25° and 46° exhibit no maxima, but are very nearly straight lines. T. H. P.

Reduction with Platinum and Hydrogen at the Ordinary Temperature. I. Richard Willstätter and Erwin W. Mayer (*Ber.*, 1908, 41, 1475—1480).—Reductions by means of hydrogen, which in presence of nickel or cobalt take place at high temperatures (Sabatier and Senderens, Abstr., 1905, i, 333), may be accomplished at the ordinary temperature in presence of platinum (Fokin, Abstr., 1907, i, 819). This method is of special importance for the reduction of olefines which are volatile only with difficulty. The application of the method to the reduction of a number of substances, including that of benzoic acid to hexahydrobenzoic acid, is described. The following facts are new.

Erucyl alcohol, $C_{22}H_{44}O$, m. p. 34·5°, prepared from erucic acid by Bouveault and Blanc's method (Abstr., 1904, i, 642), forms a *dibromide*, m. p. 45—45·5°, and on reduction yields *docosyl alcohol*, $C_{22}H_{46}O$, m. p. 71—71·5°. The *urethane* of the saturated alcohol has m. p. 86—86·5°.

Reduction of geraniol leads to the formation of the saturated alcohol in a 40% yield, and of $\beta\zeta$-dimethyloctane, $C_{10}H_{22}$, in a 60% yield. The hydrocarbon is a colourless oil, b. p. 156·5—158°/724 mm., D_4^0 0·741, D_4^{20} 0·730, and is probably identical with Markownikoff and Reformatsky's hydrocarbon (Abstr., 1893, i, 662).

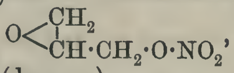
Dihydrophytol, $C_{20}H_{42}O$, formed together with phytane by reduction of phytol, is a colourless oil, b. p. 201·5—202°/9·5 mm., D_4^0 0·849. G. Y.

[General Method for the Preparation of Fatty or Aromatic Primary Ethers.] Albert Reychler (*Bull. Soc. chim.*, 1908, [iv], 3, 551).—A reply to Hamonet (this vol., i, 242), admitting the accuracy of the latter's claim for priority in the discovery that the action of chlorodimethyl ether on magnesium alkyl haloids is capable of general application in the preparation of primary ethers.

T. A. H.

Glyceryl Nitrates. WILHELM WILL [with HAANEN and STÖHRER] (*Ber.*, 1908, **41**, 1107—1125. Compare Mikolajczak, *Glückauf*, 1904, 629).—A comparative study of the mono-, di-, and trinitrates of glycerol. It is shown that, contrary to the statement of Mikolajczak, no advantages would accrue from the commercial employment of the dinitrate in place of the trinitrate, since the former in the anhydrous state is almost as explosive as the latter, and is as liable to freeze at low temperatures as the trinitrate, since it absorbs water from the air, forming a solid hydrate. The product formed by adding 100 parts of glycerol to 500 parts of a mixture of 45 parts of water, 342 parts of sulphuric acid, and 113 parts of nitric acid, or by adding glycerol to nitric acid (1·50), or by diluting a solution of glyceryl trinitrate in concentrated sulphuric acid with water, is a mixture of glyceryl $\alpha\beta$-dinitrate and glyceryl $\alpha\gamma$-dinitrate. The mother liquor from the action of nitric acid (1·50) on glycerol yields, on concentration and extraction with ether, an oil consisting of a mixture of glyceryl α-mononitrate and glyceryl β-mononitrate.

Glyceryl $\alpha\gamma$-dinitrate, $OH\cdot CH(CH_2\cdot O\cdot NO_2)_2$, is an oil, b. p. 146—148°/15 mm. (decomp.), D_{15}^{15} 1·47, which solidifies at $-40°$ and softens at $-30°$. It readily absorbs water from the air, forming a *hydrate*, $3(C_3H_6O_7N_2),H_2O$, crystallising in large, transparent, colourless prisms, m. p. 26°, b. p. 145°/15 mm. (decomp.). The anhydrous substance is almost as explosive as glyceryl trinitrate, but is far less sensitive to concussion in the hydrated form. Both forms detonate when heated on platinum foil. The *benzoate*, $OBz\cdot CH(CH_2\cdot O\cdot NO_2)_2$, is a crystalline substance, m. p. 67°; the p-*nitrobenzoate*, $C_{10}H_9O_{10}N_3$, crystallises in small pyramids, m. p. 94°.

Glyceryl $\alpha\beta$-dinitrate, $NO_2\cdot O\cdot CH_2\cdot CH(O\cdot NO_2)\cdot CH_2\cdot OH$, is an oil, b. p. about 145°/15 mm. (decomp.); the *hydrate* is also an oil; both forms are very similar in physical properties to the corresponding $\alpha\gamma$-dinitrates. The *benzoate* and *acetate* could not be obtained in a crystalline form; the p-*nitrobenzoate* crystallises in yellow, rhombic leaflets, m. p. 81°. Both dinitrates yield on treatment with alkali hydroxides the same *mononitroglycide*,  $O\Big<\begin{matrix}CH_2\\ |\\ CH\cdot CH_2\cdot O\cdot NO_2\end{matrix}$, a colourless, limpid liquid, D_{20}^{20} 1·332, b. p. 174° (decomp.).

Glyceryl α-mononitrate, $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot NO_2$, is formed when mononitroglycide is heated for some time with water; it crystallises in long prisms, m. p. 58—59°, b. p. about 155—160°/15 mm., and is very similar to glycerol in its general properties. It is not explosive, and yields on nitration a mixture of the trinitrate, $\alpha\beta$-dinitrate, and $\alpha\gamma$-dinitrate. It forms with calcium nitrate a crystalline *double* salt, $4NO_2\cdot O\cdot C_3H_5(OH)_2,Ca(NO_3)_2$, m. p. 117°. The *diacetate*, $OAc\cdot CH_2\cdot CH(OAc)\cdot CH_2\cdot O\cdot NO_2$, has m. p. 18—20°; the *dibenzoate*, $OBz\cdot CH_2\cdot CH(OBz)\cdot CH_2\cdot O\cdot NO_2$, crystallises in colourless needles, m. p. 68—69°; the *di*-p-*nitrobenzoate* forms yellowish-white crystals, m. p. 139°.

Glyceryl β-mononitrate, $NO_2\cdot O\cdot CH(CH_2\cdot OH)_2$, crystallises in slender leaflets, m. p. 54°, b. p. about 155—160°/15 mm. It is very similar in properties to the α-mononitrate, but does not form a double salt with calcium nitrate. It is converted on nitration into the trinitrate and the αβ-dinitrate; the *di*-p-*nitrobenzoate* crystallises in yellow prisms, m. p. 152°. W. H. G.

The Stability of Lecithin. John H. Long (*J. Amer. Chem. Soc.*, 1908, **30**, 881—895).—In the work of previous authors on the lecithins, it has generally been assumed that these substances readily undergo decomposition. In the course of an investigation, information was needed on this point, and experiments were therefore carried out which led to the following results.

Aqueous emulsions of egg and brain lecithin are very slightly affected by light, and are comparatively stable with respect to temperature. An increase of temperature or prolonged heating does not increase the dissociation as measured by acidity and electrical conductivity. Lecithin emulsions have an acid reaction. The residues, left after precipitating the emulsions with acetone, however, form neutral emulsions with water. On precipitating lecithin by the addition of acetone to an ethereal solution, in the process of preparation, a product is obtained which becomes acid when treated with water. The precipitation from water by means of acetone appears to cause some decomposition, as indicated by a change in the ratio of phosphorus to nitrogen in the residue. It is probable that the acidity is not due to the lecithin itself, but to decomposition products. Emulsions of both egg and brain lecithin are readily precipitated by dilute salt solutions, but no relation is observable between the precipitating powers of the salts and the valencies of their ions. E. G.

Behaviour of Emulsions of Lecithin with Metallic Salts and Certain Non-Electrolytes. John H. Long and Frank Gephart (*J. Amer. Chem. Soc.*, 1908, **30**, 895—902).—Solutions of many salts and acids cause precipitation when added to weak aqueous emulsions of lecithin. The completeness of the precipitation does not seem to bear any relation to the valency of the cations, but is connected in some way with the degree of dissociation of the various compounds. It has been found that ether and similar solvents extract very little lecithin from the pure emulsions, but that, after the addition of salt solutions, the lecithin is immediately taken up by the solvent; this action of the salts is related to their precipitating power. Certain non-electrolytes, such as glycerol, dextrose, sucrose, and carbamide, neither cause precipitation from the emulsions nor aid the solution of the lecithin by ether; on the addition of traces of salt solutions to the mixtures, however, the lecithin is immediately dissolved by the ether.
E. G.

Methods for the Preparation of Lecithin and other Phosphatides from Plant Seeds. Ernst Schulze (*Zeitsch. physiol. Chem.*, 1908, **55**, 338—351).—The powdered material is extracted with 95%

alcohol at 50°, and the solvent is distilled off at the same temperature. The residue is treated alternately with water and ether, and the aqueous and ethereal extracts are brought (without shaking) into a separating funnel. The layers readily separate on addition of salt. The ethereal extract, after drying with anhydrous sodium sulphate, is evaporated down, and the residue taken up with acetone, in which the lecithin is insoluble; in this way, the fat is separated from the lecithin and phosphatides. The latter are then dissolved in ether, and precipitated from the concentrated solution by means of methyl acetate. The preparations thus obtained generally contain a certain amount of carbohydrates. S. B. S.

Action of Methyl Sulphate on Alkali Polysulphides. Wilhelm Strecker (*Ber.*, 1908, **41**, 1105—1106).—Attempts to purify the hydrogen persulphides investigated by Bruni and Borgo (this vol., ii, 102) by distillation under reduced pressure having proved unsuccessful, the more stable methyl derivatives have been prepared by the action of methyl sulphate on alkali polysulphides.

Methyl trisulphide, Me_2S_3 (compare Klason, Abstr., 1888, 356), is obtained by the distillation under reduced pressure of the products formed by the action of methyl sulphate on the alcoholic solutions of sodium pentasulphide, tetrasulphide, or trisulphide. It has not yet been definitely settled whether compounds are first formed having the composition Me_2S_5 or Me_2S_4, and on distillation decompose, yielding the trisulphide. W. H. G.

Catalytic Reactions at High Temperatures and Pressures. XXII. Catalytic Decomposition of Acids. Wladimir N. Ipatieff (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 514—518).—The author has investigated the decomposition of acetic acid which occurs when its vapour is passed over heated zinc, zinc oxide, zinc carbonate, calcium carbonate, strontium carbonate, barium carbonate, sodium hydroxide, sodium carbonate, or iron. The acid undergoes decomposition in two distinct ways, in one of which acetone, water, and carbon dioxide are formed, and in the other, hydrocarbons and hydrogen. At the moment of its formation, the acetone may undergo decomposition into carbon monoxide and saturated and unsaturated hydrocarbons. The carbonates of barium, strontium, calcium, and zinc, and also zinc oxide and metallic zinc, produce mainly the ketonic decomposition of acetic acid. The first action of the acetic acid may be to form metallic acetate, which then decomposes, giving acetone and the carbonate of the metal. When sodium hydroxide is used, the yield of acetone is small and that of methane large, whilst when sodium carbonate is employed, a considerable amount of acetone is formed. When iron is used as catalyst, only traces of acetone are obtained, the gases formed consisting of carbon dioxide and monoxide, hydrogen, methane, and ethylene hydrocarbons. T. H. P.

Preparation of Soluble Basic Acetates of Aluminium, Chromium, and Iron. E. de Haën (D.R.-P. 190451).—The basic acetates of aluminium, chromium, and iron may be obtained in soluble stable form when to a strong solution of their sulphates and sodium acetate sufficient alkali is added to produce either of the following basic salts : $M'''_2(OH)_2(C_2H_3O_2)_4$ or $M'''_2(OH)_3(C_2H_3O_2)_3$. The solution should be sufficiently concentrated to keep the sodium sulphate produced in the form of a saturated solution at 34°.

A powdered mixture (19 parts) containing 71·3% of crystallised sodium acetate and 28·6% of anhydrous sodium carbonate is added to 64·7 parts of an aqueous solution of sodium alum (34°Bé) containing 17·6% of aluminium at 55°. After stirring for thirty minutes, the *basic aluminium acetate*, $Al_2(OH)_3(C_2H_3O_2)_3$, was centrifugalised and dried at moderate temperatures.

The *basic chromium* and *ferric acetates*, $Cr_2(OH)_3(C_2H_3O_2)_3$ and $Fe_2(OH)_3(C_2H_3O_2)_3$, are similarly prepared; the latter is a brick-red substance. G. T. M.

Certain Volatile and Non-volatile Compounds formed in Rancid Fats. ALBERTO SCALA (*Gazzetta*, 1908, **38**, i, 307—327. Compare Abstr., 1899, i, 478).—Oil and lard which had been kept for some years until they had become thoroughly rancid were found to contain formic, butyric, hexoic, heptoic, and nonoic acids, and butaldehyde, hexaldehyde (?), heptaldehyde, and nonaldehyde. The odour and flavour of rancid fats are due, in some degree, to the hexaldehyde (?) and butaldehyde, but mainly to the heptaldehyde and nonaldehyde. The methods by which the various constituents were separated and characterised are fully described. T. H. P.

Action of Ozone on Triple Linkings. CARL D. HARRIES (*Ber.*, 1908, **41**, 1227—1232).—Polemical (compare Molinari, Abstr., 1907, i, 1039; this vol., i, 244; Harries, this vol., i, 75). E. F. A.

Formation of Esters by Mass Action of Anions. BROR HOLMBERG (*Ber.*, 1908, **41**, 1341—1346).—It has been already shown that the decomposition of ethyl diazoacetate by dilute acids is retarded by neutral salts, such as chlorides, sulphates, or nitrates (Fraenkel, Abstr., 1907, ii, 746), and Bredig and Ripley, from a study of the decomposition in the presence of chlorides, drew the conclusion that the ratio of the formation of ethyl chloroacetate to ethyl diazoacetate decomposition increased with the concentration of the chlorine ions, but was independent of the concentration of diazoacetate or hydrogen ions (Abstr., 1907, ii, 941).

This view is supported by the isolation of ethyl glycollate and its nitric ester when the decomposition is carried out in the presence of sodium nitrate, and by fractional crystallisation of the liquid obtained after the decomposition of the diazoacetate in the presence of sodium sulphate and extraction with ether, when a salt was finally obtained which crystallised from alcohol in silky white leaflets, and proved to be *sodium ethyl glycollate sulphate*, $OEt{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}SO_3Na$.

The reaction with nitrates and sulphates has also been studied quantitatively, with the result that the best yield of glycollic ester is obtained when the temperature is low and the concentration of anions is as great as possible. W. R.

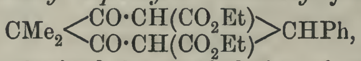
Condensations with Ethyl Acetoacetate and their Reversion. WALTER DIECKMANN and ARTHUR KRON (*Ber.*, 1908, **41**, 1260—1278). —In a previous communication (Abstr., 1900, i, 623), the decomposition of αγ-dicarbonyl compounds by sodium ethoxide was shown to depend on their acidity. The stability of esters of β-ketocarboxylic acids, previously established, is now shown to extend to non-substituted αγ-diketones, as typified by benzoylacetone. The stability of cyclic ethyl succinylsuccinate towards sodium ethoxide illustrates how the increase in acidity raises the stability. The catalytic hydrolysis of esters of dialkylated β-ketocarboxylic acids has been confirmed in the cases of ethyl dibenzylacetoacetate and the alkylated propionylpropionic acid esters.

Compounds such as ethyl *as*-dimethylacetonedicarboxylate,

$$CO_2Et{\cdot}CMe_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et,$$

and methyl γ-acetyldimethylacetoacetate,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Me,$$

which contain an acid salt-forming group, $CO{\cdot}CH_2{\cdot}CO$, alongside a neutral, in itself decomposable, nucleus, $CO{\cdot}CR_2{\cdot}CO$, are hardly attacked by excess of sodium ethoxide even on boiling. On the other hand, when the strongly acid 1 : 3-dicarbonyl group, $CO{\cdot}CH_2{\cdot}CO$, is converted by alkylation into the less acid group, $CO{\cdot}CHR{\cdot}CO$, the stability towards sodium ethoxide disappears, as exemplified by the behaviour of ethyl trimethylacetonedicarboxylate. The group $R_2{:}CH{\cdot}CO$ will permit of the ester condensation, provided salt formation takes place at the same time and opposes the decomposition in the reverse direction by the sodium alkoxide. Such condensations have been observed in the case of the interaction of sodium ethylmalonate and benzylidenemethyl *iso*propyl ketone and of ethyl sodio*iso*butyrylacetate and ethylcinnamic acid, when products which give colorations with ferric chloride are formed, but have not been isolated. In the case, however, of ethyl benzylidenemalonate and ethyl *iso*butyrylacetate, the product *ethyl* 4-*phenyl*-1 : 1-*dimethyl*cyclo*hexane*-2 : 6-*dione*-3 : 5-*dicarboxylate*,  $CMe_2{<}\begin{matrix}CO{\cdot}CH(CO_2Et)\\CO{\cdot}CH(CO_2Et)\end{matrix}{>}CHPh$, is formed. The same compound is obtained by methylation of ethyl phenylhydroresorcinoldicarboxylate, whereby the constitution is established.

Ethyl dibenzylacetoacetate, on boiling for three hours with alcoholic sodium ethoxide, yields ethyl dibenzylacetate, a colourless oil, b. p. 196—198°/14 mm., which could not be brought to crystallisation, but was identified by conversion into dibenzylacetic acid, m. p. 89—90°. *Methyl dibenzylacetate* forms colourless needles, m. p. 40—41°. The compound m. p. 88—89°, described as ethyl dibenzylacetate by Fichter and Schiess (Abstr., 1901, i, 544), is regarded as more probably the ester $CO_2Et{\cdot}C(CH_2{\cdot}C_6H_5)_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$.

Ethyl benzylidenebenzoylacetate is decomposed on heating for three hours with alcoholic sodium ethoxide into ethyl benzoate and ethyl cinnamate. On the other hand, benzoylacetone, ethyl succinylsuccinate, ethyl γ-acetyl-α-dimethylacetoacetate, and ethyl *as*-dimethylacetonedicarboxylate are all unchanged by boiling for three hours with sodium ethoxide.

Ethyl propionylpropionate is a colourless oil, b. p. 87—88°/16 mm.;

it can be alkylated by methyl iodide and sodium ethoxide to ethyl propionylethylpropionate, a colourless oil, b. p. 97—98°/16 mm. *Ethyl propionylbenzylpropionate*, $\mathrm{COEt \cdot CMe(C_7H_7) \cdot CO_2Et}$, prepared by the action of benzyl chloride or bromide, is a colourless oil, b. p. 179—183°/20—21 mm. Boiling with sodium ethoxide converts this into *ethyl α-benzylpropionate*, $\mathrm{CH_3 \cdot CH(C_7H_7) \cdot CO_2Et}$, a colourless oil, b. p. 142—143°/20—21 mm.

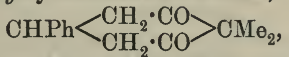
Ethyl sodio*iso*butyrylacetate in ethereal solution condenses with ethyl benzylidenemalonate to form *ethyl 4-phenyl-*1 : 1*-dimethyl*cyclo*hexane-*2 : 6*-dione-*3 : 5*-dicarboxylate*, crystallising in colourless prisms, m. p. 146°. This gives a bluish-violet coloration with ferric chloride, and forms a green, crystalline *copper* salt and a *bisphenylpyrazolone* derivative, $\mathrm{C_{28}H_{24}O_2N_4}$, separating in colourless crystals which were not melted at 270°.

Ethyl *iso*butyrylacetate interacts with benzylideneacetophenone in presence of sodium ethoxide, forming *ethyl γ-benzoyl-α-*iso*butyryl-β-phenylbutyrate*, of which the colourless crystals have m. p. 112°.

Ethyl 4-p*-methoxyphenyl-*1 : 1*-dimethyl*cyclo*hexane-*2 : 6*-dione-*3 : 5*-dicarboxylate*, prepared from ethyl anisylidenemalonate, has m. p. 141°.

The above phenyl*cyclo*hexanedione ester compound dissolves in methyl-alcoholic potassium hydroxide, and separates in the form of a sparingly soluble crystalline *dipotassium* salt. If left in contact with the potassium hydroxide, this salt passes into solution, and separates again in the form of colourless crystals of a *potassium* salt of a *tricarboxylic acid*, formed by opening the ring. Decomposed with mineral acids, the salt yields a thick, colourless oil, giving no coloration with ferric chloride. The ester is quite stable towards sodium ethoxide. Heating with mineral acids converts it into γ-iso*butyryl-β-phenylbutyric acid*, which crystallises in colourless needles, m. p. 106—107°. The *amide* forms colourless crystals, m. p. 126°; the semicarbazone has m. p. 165°.

4*-Phenyl-*1 : 1*-dimethyl*cyclo*hexane-*2 : 6*-dione*,



$$\mathrm{CHPh}{<}\begin{matrix}\mathrm{CH_2 \cdot CO}\\ \mathrm{CH_2 \cdot CO}\end{matrix}{>}\mathrm{CMe_2},$$

prepared by heating the above ester with 80% acetic acid, forms long, colourless needles, m. p. 86°; the *dioxime* has m. p. 235—236°; the *bisphenylhydrazone* forms faintly yellow prisms, m. p. 175—176°.

Ethyl 4*-phenyl-*1*-ethyl*cyclo*hexane-*2 : 6*-dione-*3 : 5*-dicarboxylate* forms colourless crystals, m. p. 146°, and gives an intense brownish-violet coloration with ferric chloride.

Ethyl 3-iso*butyryl-*2 : 6*-diphenyl-*4-iso*propyl-*Δ^3-cyclo*hexene-*1 : 1*-dicarboxylate*, prepared by the condensation of 2 mols. of benzylidenemethyl *iso*propyl ketone and 1 mol. of ethyl sodiomalonate, crystallises in colourless needles, m. p. 190°, and shows no coloration with ferric chloride.

The *dibromide* of benzylidenemethyl *iso*propyl ketone crystallises in prisms, m. p. 102—103°.

Ethyl 3*-benzoyl-*2 : 4 : 6*-triphenyl-*Δ^3-cyclo*hexene-*1 : 1*-dicarboxylate*, similarly prepared from benzylideneacetophenone, forms colourless crystals, m. p. 197°. E. F. A.

Condensations with Cinenic Acid. HANS RUPE and CARL LIECHTENHAN (*Ber.*, 1908, 41, 1278—1286).—By the action of concentrated sulphuric acid on cinenic acid, two products are formed: a liquid acid, $C_9H_{16}O_3$, which yields *aa*-dimethylglutaric acid,

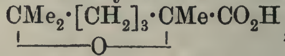
$$CO_2H\cdot CH_2\cdot CH_2\cdot CMe_2\cdot CO_2H,$$

on oxidation with nitric acid, and *aa*-dimethyladipic acid,

$$CO_2H\cdot [CH_2]_3\cdot CMe_2\cdot CO_2H,$$

together with bromoform on treatment with sodium hypobromite, and is therefore a *δ-acetyl-aa-dimethyl*-n-*valeric acid*,

$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot CO_2H.$$

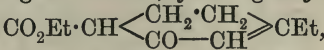
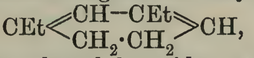
This change involves wandering of a methyl from carbon atom ζ to carbon atom *a* in cinenic acid,  $\underbrace{CMe_2\cdot[CH_2]_3\cdot CMe}_{O}\cdot CO_2H$, and is explained by the intermediate formation of a ring. The second product formed in small quantities is a cyclic lactone, $C_9H_{14}O_2$, probably the lactone of 1 : 3-dimethyl*cyclo*hexan-1-ol-3-carboxylic acid.

Cinenic acid is prepared from methylheptenone by Rupe and Schlochoff's method (Abstr., 1905, i, 409), and fuller details of its preparation are now given. When dissolved in cooled concentrated sulphuric acid, it is converted into *δ-acetyl-aa-dimethyl*-n-*valeric acid*, a colourless liquid, which has b. p. 275—280°/739 mm., 168·8—169·4°/11·5 mm., D_4^{20} 1·0211, n_D^{20} 1·44883. The *ethyl* ester has b. p. 121·5°/12·5 mm. The *semicarbazone* forms large, colourless, many-faced crystals, m. p. 165°; the *oxime* separates in large, hard, prismatic prisms, m. p. 93—93·5°. By oxidation with nitric acid, *aa*-dimethylglutaric acid is formed, m. p. 84°, and is identified by means of the anhydride, *p*-toluidide, and anilide.

The *lactone* of 1 : 3-*dimethyl*cyclo*hexan*-1-ol-3-*carboxylic acid* has b. p. 102—114°/11 mm., and forms crystals, m. p. 50—51°. The *calcium* salt of the hydroxy-acid crystallises in hexagonal plates. With bromine, a crystalline product, m. p. 73·5—74°, is formed, which yields the original lactone when heated with alcoholic potassium hydroxide. E. F. A.

Dehydracetic Acid. OSWALD HESSE (*J. pr. Chem.*, 1908, [ii], 77, 390—392).—An acid, m. p. 108°, obtained on recrystallising rhein from ethyl acetoacetate and thought to be a derivative of rhein (Abstr., 1906, i, 280), has proved to be dehydracetic acid. A number of its salts are described. The *phenylmethylhydrazide*, $C_{15}H_{16}O_3N_2$, crystallises in light yellow needles, m. p. 148°. G. Y.

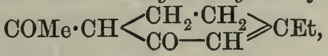
Syntheses by means of β-Chloroethyl and Vinyl Ketones. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 413—421, 421—427. Compare this vol., i, 418).—Vorländer has shown (Abstr., 1897, i, 272) that it is possible to attach the sodium derivatives of β-ketonic esters to unsaturated acids. In the present paper, this work is extended to unsaturated ketones, and a number of products so obtained are described. When the vinyl ketones are employed directly, the yields of the products sought are unsatisfactory, and it is more convenient to condense the chloro-derivatives of the corresponding saturated ketones with the sodium derivatives of the β-ketonic substances used.

*Ethyl α-acetyl-γ-propionyl-*n*-butyrate*, $COEt\cdot CH_2\cdot CH_2\cdot CHAc\cdot CO_2Et$, b. p. 150°/8 mm. (decomp.), obtained by condensing the sodium derivative of ethyl acetoacetate with β-chloroethyl ethyl ketone, is a mobile liquid with a slight odour of mint, gives a bluish-violet colour with ferric chloride, yields a *disemicarbazone*, m. p. 195° (decomp.), and, unlike the δ-diketones described by Knoevenagel (Abstr., 1893, i, 419), is relatively stable, not undergoing ring condensation by the action of heat, sulphuric acid in alcohol, or sodium ethoxide, but only when its solution in ether is saturated with hydrogen chloride, yielding *ethyl 1-ethyl-*Δ^1-cyclo*hexene-3-one-4-carboxylate*,  $CO_2Et\cdot CH<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CO—CH}>CEt$, b. p. 150°/14 mm., a liquid giving a blue coloration with ferric chloride, and possessing a pleasant mint-like odour. Its *semicarbazone*, m. p. 207°, crystallises from alcohol. When warmed with diluted sulphuric acid, the cyclic ester yields 1-*ethyl*-Δ^1-cyclo*hexene*-3-*one*, b. p. 83°/8 mm., which is pungent and mint-like in odour, and gives a *semicarbazone*, m. p. 240° (decomp.). With 1 mol. of hydroxylamine hydrochloride, it furnishes a crystalline *oxime*, m. p. 106°, and with 2 mols. an oil (compare Hagemann, Abstr., 1893, i, 393). The ethyl*cyclo*hexenone reacts with magnesium ethyl bromide to form 1 : 3-*diethyl*cyclo*hexadiene*,  $CEt<\genfrac{}{}{0pt}{}{CH—CEt}{CH_2\cdot CH_2}>CH$, b. p. 68°/9 mm. pressure, and with magnesium phenyl bromide to form 1-*phenyl*-3-*ethyl*cyclo*hexadiene*, b. p. 126—128°/8 mm. pressure, which has an odour like that of diphenyl.

When the sodium derivative of acetylacetone is condensed with β-chloroethyl ethyl ketone, there is formed the *triketone*,

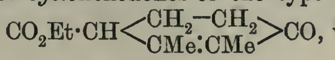
$$CHAc_2\cdot CH_2\cdot CH_2\cdot COEt,$$

b. p. 154°/16 mm., a faintly yellow liquid, which gives a bluish-violet coloration with ferric chloride, and with 3 mols. of semicarbazide hydrochloride yields a *carbamylpyrazolesemicarbazone*, which decomposes at 190°. On saturation of its solution in ether with hydrogen chloride, the triketone forms 4-*acetyl*-1-*ethyl*-Δ^1-cyclo*hexene*-3-*one*,



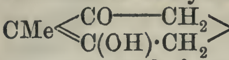
$$COMe\cdot CH<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CO—CH}>CEt,$$

b. p. 144°/15 mm., a faintly yellow liquid, giving a blue coloration with ferric chloride, and yielding a *carbamylpyrazole*, m. p. 165° (decomp.), which separates from alcohol in dense crystals, and a *dioxime*, m. p. 216° (decomp.), which crystallises from ethyl acetate in brilliant needles.

The two δ-ketonic esters, referred to above, when undergoing cyclic condensation in presence of hydrochloric acid, form, in addition to substituted *cyclo*hexenones of the type described, isomeric products of the type  $CO_2Et\cdot CH<\genfrac{}{}{0pt}{}{CH_2—CH_2}{CMe:CMe}>CO$, which are usually produced in too small quantities to be isolated.

The sodium derivative of ethyl malonate condenses with β-chloroethyl ethyl ketone to form *ethyl propionylethylmalonate*,

$$COEt\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2,$$

b. p. 166°/14 mm. pressure, a viscid liquid of peculiar odour, furnishing a *semicarbazone*, m. p. 90°, which crystallises in cottony needles from warm ether. The *free acid*, m. p. 83°, crystallises from cold benzene, and when heated at 160° furnishes *γ-propionylbutyric acid*, m. p. 50°, which crystallises from ether on addition of light petroleum, and yields a *semicarbazone*, m. p. 196°, and an *oxime*, m. p. 118°. *Methyl γ-propionylbutyrate*, b. p. 101—102°/10 mm., has but little odour. The *ethyl* ester, b. p. 116°/14 mm., on treatment by Vorländer's method (*loc. cit.*), furnishes a nearly theoretical yield of 1-*methyl*-Δ^1cyclo*hexen*-2-*ol*-6-*one*,  $CMe\lt\begin{matrix}CO\text{——}CH_2\\C(OH)\cdot CH_2\end{matrix}\gt CH_2$, m. p. 210° approx. (decomp.). This forms opaque crystals from alcohol, and furnishes with semicarbazide hydrochloride a *carbamylpyrazole*, which crystallises from formic acid on addition of alcohol and decomposes without melting, and a *dioxime*, m. p. 220° (approx.), which separates from alcohol in slender needles.

1-Methyl-Δ^1-*cyclo*hexen-2-ol-6-one differs markedly in solubility from dihydroresorcinol, but comparison of the specific refractive powers of the two substances (respectively 0·28996 and 0·28516 in alcohol for sodium light) indicates that they are similarly constituted. The higher homologue gives a faint blue coloration with ferric chloride in the cold, but a much more intense colour is produced if the reagent is added to a hot saturated solution (0·3%) of the substance in water.

T. A. H.

Reactions of Mercuric Chloride with Organic Acids. William Oechsner de Coninck and Dautry (*Bull. Acad. roy. Belg.*, 1908, 55—56).—The authors confirm Becquerel and Marchand's observation that solutions containing mercuric chloride, oxalic acid, and water deposit mercurous chloride on exposure to sunlight for a few hours. When malonic acid is substituted for oxalic acid, traces of precipitation occur after about twelve days. It is suggested that this difference in reaction may be used as a method of distinguishing between the two acids.

T. A. H.

Some Cuprammonium Salts. VI. David W. Horn and Minnie A. Graham (*Amer. Chem. J.*, 1908, **39**, 505—513).—In an earlier paper (Abstr., 1906, ii, 231), a stable cuprammonium oxalate, $CuC_2O_4,2NH_3$, was described. It has now been found that a labile isomeric salt exists. The former is termed the α-, and the latter the β-compound.

The α-salt forms deep sapphire-coloured crystals, is saturated towards ammonia, has D_4^{25} 2·305, and dissociates at about 187°/30 mm. with production of a dark olive-green *compound*.

The β-salt is a sky-blue, amorphous substance, is unsaturated towards ammonia, has D_4^{25} about 2·230, dissociates at about 171°/30 mm. with formation of a green compound, and when heated at 100° is more or less completely transformed into the α-salt.

E. G.

Constitution of Carbon Suboxide. Otto Diels and Paul Blumberg (*Ber.*, 1908, **41**, 1233—1236).—Polemical (compare Michael, this vol., i, 316; also Diels and Blumberg, this vol., ii, 103; Abstr., 1906, ii, 227; 1907, ii, 180). The following reasons are given in favour of adopting the symmetrical allene formula CO:C:CO. (1) Boiling point +7°, (2) similarity with the metal carbonyls, (3) high value of the molecular refraction and dispersion, (4) analogy to keten, (5) addition of 4 atoms of bromine and formation from dibromomalonyl bromide, (6) formation of malonic acid on the addition of water, and (7) improbable existence of a β-lactone containing a triple linking. E. F. A.

Preparation of Adipic Acid and of Ethyl *cyclo*Pentanonecarboxylate. Louis Bouveault and Réné Locquin (*Bull. Soc. chim.*, 1908, [iv], 3, 437—441).—Adipic acid may be prepared by the oxidation of *cyclo*hexane (Aschan, Abstr., 1899, i, 672), but the process is very slow, and *cyclo*hexanol, which may be prepared in large quantity by reducing phenol by Sabatier and Senderens' method, is a more satisfactory starting point. A detailed description is given of the method of preparing adipic acid by oxidation of *cyclo*hexanol with hot nitric acid, and of separating the acid from oxalic, glutaric, and succinic acids simultaneously formed. The yield of adipic acid is 52% of the theoretical. Ethyl adipate dissolved in benzene is readily converted by the action of sodamide (compare Haller, Abstr., 1904, i, 600) into ethyl *cyclo*pentanone-2-carboxylate, and the preparation of this substance and its separation from *cyclo*pentanone, simultaneously formed, is described in detail. T. A. H.

Bismuth Cholate. Emil Wörner (D.R.-P. 191385).—Bismuth cholate is prepared by heating any basic bismuth salt with excess of an aqueous solution of an alkali cholate. The product is a yellowish-white insoluble basic salt, the composition of which depends on that of the bismuth salt employed in its production; alcohol decomposes it, withdrawing cholic acid. G. T. M.

The Asymmetric Conjugation of Glycuronic Acid. Paul Mayer (*Biochem. Zeitsch.*, 1908, 9, 439—441).—Inactive camphor was administered to a dog, and the excreted glycuronate was isolated from the urine. This on hydrolysis yielded a campherol, in which $[\alpha]_D^{17} = -5{\cdot}91°$. Pure *l*-campherol gives $[\alpha]_D\ -32{\cdot}91°$. Hence the campherol in the urine contained 17·9% of the active variety, and an asymmetric conjugation with glycuronic acid had taken place in the organism. S. B. S.

Formaldehyde Solutions. Marcel Delépine (*Bull. Soc. chim.*, 1908, [iv], 3, 411—413).—The author asserts that certain of the conclusions regarding the constitution of aqueous solutions of formaldehyde drawn by Auerbach and Barschall from the results of their investigations (Abstr., 1905, i, 860; 1908, i, 131) are merely confirmatory of views already published by him (Abstr., 1897, i, 504, 505; ii, 359). T. A. H.

A Simple Reaction for Producing a Disinfectant Gas. [Formaldehyde Vapour.] G. Carteret (*Compt. rend.*, 1908, 146, 819—820).—Reactions hitherto described for the production of formaldehyde by the action of peroxides or per-salts on trioxymethylene or paraformaldehyde suffer under the disadvantage of being either too violent or too slow. But by the action of water (3 parts) on a mixture of bleaching powder (2 parts) with paraformaldehyde (1 part), a rapid evolution of formaldehyde vapour is produced, the temperature of the mixture rising to 108°. The gas evolved contains only traces of chlorine, and does not attack objects placed in it, except certain aniline dyes which react with formaldehyde. Its bactericidal power is very great. Sporulated charcoal placed under two thicknesses of cloth is sterilised in seven hours in the atmosphere produced by 125 grams of paraformaldehyde in a space of 20 cubic metres. In this and similar reactions, the author considers the production of formaldehyde to be due to the elevation of temperature in the presence of water vapour. E. H.

Keten. Hermann Staudinger and Helmut W. Klever (*Ber.*, 1908, **41**, 1516—1517).—A reply to Wilsmore and Stewart (this vol., i, 318). G. Y.

Saccharin and Alkali Saccharinates. Eberhard Rimbach and Edmund Heiten (*Annalen*, 1908, **359**, 317—335).—Tables are given of the optical rotation and rotatory dispersion of saccharin in water, methyl and ethyl alcohols, and acetone, and of alkali saccharinates in water, the influence of concentration and temperature being also observed. The crystallographic constants are also given, as well as the electrical conductivity of the aqueous solutions of the potassium and rubidium salts. J. V. E.

The Relation of the Cyclic Inosite to the Aliphatic Sugars. Carl Neuberg (*Biochem. Zeitsch.*, 1908, **9**, 551—556).—Inosite on distillation with phosphoric oxide or boron trioxide yields furfuraldehyde, which was identified by the isolation of its condensation products with thiosemicarbazide and *p*-nitrophenylhydrazine. This reaction indicates a relationship with the aliphatic sugars. S. B. S.

Constitution of "Phytin." Carl Neuberg (*Biochem. Zeitsch.*, 1908, **9**, 557—560).—Phytin is a condensation product of inosite and phosphoric acid, not of formaldehyde and phosphoric acid, since on distillation with glacial phosphoric acid it yields a liquid which, on rectification, gives the ordinary furfuraldehyde reactions (preceding abstract). S. B. S.

Action of Anhydrous Nitric and Sulphuric Acids on Cellulose. Berthold Rassow and Waldemar von Bongé (*Zeitsch. angew. Chem.*, 1908, **21**, 732—737).—The mixture of nitric and sulphuric acids employed for the commercial nitration of cellulose always contains a certain amount of water. In the present communication, the action of a mixture of anhydrous acids has been studied; by keeping the acids in large excess, the influence of the water formed by the reaction was as far as possible eliminated. It was found that esters of nitric acid, insoluble in water, were only formed when the nitrating mixture contained at least one part of nitric acid to seven of sulphuric acid; the resulting nitrocellulose is short fibred and contains 37·79% of unchanged cellulose. By increasing the proportion of nitric acid, the percentage of nitrogen in the resulting product was raised until it corresponded with a mixture of penta- and hexa-nitrocelluloses, but it never reached the figure attained with the use of the diluted acids. A sudden diminution in the nitrogen content of the nitrocellulose was observed when the proportions of acid were one of sulphuric to three of nitric, but by increasing the amount of nitric acid the percentage rose, and finally dropped again to 10·98 when nitric acid alone was employed. The nitrocellulose formed by the action of anhydrous nitric acid alone on cellulose is slimy, but on treatment with water it becomes tough. The solubility of the esters in a mixture of ether and alcohol is, on the whole, low. Contrary to the usually accepted view, it was found that nitrocelluloses are completely soluble in Schweizer's reagent on prolonged shaking. P. H.

Preparation of Amylamine. CHEMISCHE WERKE VORM. HEINRICH BYK (D.R.-P. 193166).—Leucine, when distilled under reduced pressure, furnishes amylamine, the yield depending on the degree of vacuum employed. The product contains at least two isomerides, *iso*amylamine, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$, and active amylamine, $CHMeEt \cdot CH_2 \cdot NH_2$. Owing to racemisation at the high temperature, the externally compensated form is also present. *iso*Leucine behaves similarly on distillation. G. T. M.

Preparation of Choline from Lecithin. J. D. RIEDEL (D.R.-P. 193449).—Lecithin is heated with two parts of 40% sulphuric acid, and the mixture shaken until a clear solution is obtained. On cooling, the fatty acids separate and solidify, the aqueous solution and washings are almost neutralised with barium hydroxide. The filtrate is concentrated, and the choline precipitated as its mercurichloride. This compound is suspended in water and decomposed with hydrogen sulphide, and the filtrate evaporated. The residue of choline solidifies on cooling to a yellow, crystalline mass; the melting points of the aurichloride and platinichloride from this preparation agree with those obtained formerly for these choline double salts. G. T. M.

The Quantitative Recovery of Choline from Lecithin. G. MORUZZI (*Zeitsch. physiol. Chem.*, 1908, **55**, 352—359).—By the hydrolysis of the cadmium chloride compound of lecithin with fifty times its weight of 10% sulphuric acid for four hours, scission took place of practically all the basic nitrogen (99·8%). Under these conditions, the maximum yield was obtained. Experiments were carried out with the object of quantitatively isolating the base after hydrolysis, chiefly by means of the phosphotungstate; the base was set free from the phosphotungstate, and precipitated and weighed in the form of the platinichloride. As a rule, only 77% of the choline, calculated on the nitrogen content of the scission product obtained by acid, was obtained.

S. B. S.

The Quantitative Recovery of Choline from Lecithin. Hugh MacLean (*Zeitsch. physiol. Chem.*, 1908, **55**, 360—370).—The hydrolysis was carried out by means of barium hydroxide both in aqueous solution and in solution in methyl alcohol. All the original nitrogen, except about 8%, dissolved in the alcohol. In most cases, the choline was precipitated by mercuric chloride, recovered from this precipitate, and reprecipitated as platinichloride. The amount of platinichloride recovered was only about 77% of the quantity theoretically possible (compare preceding abstract). By means of experiments carried out with pure choline, mixed with glycerophosphate and other substances, it was found that the loss is due to the incompleteness of the platinichloride precipitation, which, in the presence of substances derived from lecithin hydrolysis, amounts to about 9—10%.

S. B. S.

Compounds of Amino-acids and Ammonia. III. Peter Bergell and Johannes Feigl (*Zeitsch. physiol. Chem.*, 1908, **55**, 173—176).—By hydrolysis of diglycinimide, $NH(CO\cdot CH_2NH_2)_2$ (this vol., i, 140), with sodium hydroxide, iminodiacetic acid, $NH(CH_2\cdot CO_2H)_2$, is obtained. This acid was isolated as the crystalline *β-naphthalenesulphonyl* derivative, $C_{14}H_{13}O_6NS$, m. p. 230° (uncorr.), yielding a very sparingly soluble *barium* salt, $C_{14}H_{11}O_6NSBa$.

G. B.

Synthesis of *iso*Leucine. Felix Ehrlich (*Ber.*, 1908, **41**, 1453—1458*).—The synthesis of *d-iso*leucine described previously (Abstr., 1907, i, 592) is incomplete in so far as the initial substance is *d*-amyl alcohol, and, moreover, presents difficulties arising from the fact that commercial amyl alcohol is not an individual substance.

Bouveault and Locquin's synthesis (Abstr., 1906, i, 938) is remarkable in that, starting from inactive substances, they obtained only the racemic form of *iso*leucine, whereas theoretically the racemic form of *allo-iso*leucine should also be produced.

Taking into account the close analogy between the chemical behaviour of leucine and *iso*leucine, the author has succeeded in synthesising the racemic modification of the latter by the method successfully employed by Fischer and Schmitz (Abstr., 1906, i, 182) in the synthesis of leucine. *sec.*-Butyl iodide and ethyl sodiomalonate yield van Romburgh's *sec.*-butylmalonic acid (Abstr., 1888, 446), which by bromination by Fischer's method (Abstr., 1904, i, 890) gives *α-bromo-*sec.*-butylmalonic acid*, $CHMeEt\cdot CBr(CO_2H)_2$, m. p. 114—115° (decomp.). By distilling the latter in a vacuum, *α-bromo-β-methylvaleric acid*, $CH_3\cdot CH_2\cdot CHMe\cdot CHBr\cdot CO_2H$, is obtained, b. p. 139—140°/22 mm., which is converted by 25% ammonium hydroxide at the ordinary temperature in five days, or by concentrated ammonium hydroxide at 100° in two hours, into inactive *iso*leucine, the resolution of which by yeast will be described subsequently. C. S.

Action of Formaldehyde on the Ammonium Derivative of Ethyl Nitromalonate. A. Battaglia (*Gazzetta*, 1908, **38**, i, 356—360).—Ulpiani and Pannain (Abstr., 1903, i, 863), by the action of formaldehyde on ethyl nitromalonate in presence of ammonia, obtained an ester to which they attributed the constitution

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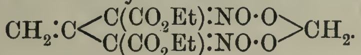
* and *Zeitsch. Ver. deut. Zuckerind.*, 1908, 528—533.



$$CH_2{:}C<\begin{array}{l}C(CO_2Et){:}NO{\cdot}O\\C(CO_2Et){:}NO{\cdot}O\end{array}>CH_2.$$

The results of the author's examination of this product are, however, best explained by the structure $NH[CH_2{\cdot}C(NO_2)(CO_2Et)_2]_2$.

The ester has the normal molecular weight in freezing benzene or boiling ether, and yields the ammonium derivative of ethyl nitromalonate when treated with dry ammonia in ethereal solution. The action of nitrous acid on the ester gives a true *nitrosoamine*,

$$C_{16}H_{24}O_{13}N_4,$$

which is obtained as a pale yellow oil, whilst with diethylamine the ester forms the *diethylamine* salt of ethyl nitromalonate, $C_{11}H_{22}O_6N_2$, m. p. 123°. The ester contains no double linking, and forms an unstable, crystalline compound with bromine. T. H. P.

Hexathiocyano-salts of Molybdenum. JOHANNA MAAS and JULIUS SAND (*Ber.*, 1908, 41, 1500—1514. Compare Abstr., 1906, i, 487; this vol., i, 11; Chilesotti, Abstr., 1906, ii, 263, 365).—The relation of the complex salts of molybdenum to the aquo-salts of the cobalt series is discussed.

The yellow, crystalline salt, previously formulated as

$$[Mo(SCN)_6(NH_3)_3(H_2O)]H_2,C_2H_4O_2,$$

is now considered to be an additive compound of acetic acid and an ammonium salt, and to have the structure

$$[Mo(SCN)_6(OH),C_2H_4O_2](NH_4)_3.$$

It crystallises in rhombic pyramides [$a : b : c = 0{\cdot}7255 : 1 : 0{\cdot}6338$], and has the electrolytic conductivity $\mu_{25} = 299{\cdot}9$ with $v = 34{\cdot}47$. The conductivity increases on addition of 1 mol. of sodium hydroxide to the aqueous solution, in consequence of the formation of sodium acetate and the ammonium salt, $[Mo(SCN)_6(OH)](NH_4)_3$; as on addition of a further 3 mols. of sodium hydroxide the sodium salt, $[Mo(SCN)_6(OH)]Na_3$, and free ammonia, which has only feeble conducting powers, are formed, the effect of the addition of the alkali does not differ greatly from that of dilution with water, and hence the conductivity of the solution diminishes, but on further addition of sodium hydroxide the conductivity again increases, as the alkali is then present in excess.

The *potassium* salt, $[Mo(SCN)_6(OH)]K_3,4H_2O$, prepared by electrolysis of potassium molybdate and thiocyanate in hydrochloric acid solution, forms yellow crystals, loses $4H_2O$ over sulphuric acid in a vacuum, has the conductivity $\mu_{25} = 355$ with $v = 64$, and when treated with acetic acid yields the *salt*, $[Mo(SCN)_6(OH),C_2H_4O_2]K_3$. This crystallises in rhombic pyramides, [$a : b : c = 0{\cdot}7124 : 1 : 0{\cdot}6318$], and has the conductivity $\mu_{25} = 334$ with $v = 64$.

The salt, $Mo(SCN)_6(OH)(HC_2H_8N_2)_3$, formed by the action of ethylenediamine on the ammonium salt, crystallises in quadratic prisms, m. p. 128° (decomp.).

The zinc salt, previously formulated as $Mo(SCN)_6Zn(NH_3)_4$, is now found to have the formula $[Mo(SCN)_6(OH)]_2Zn_3(NH_3)_{11}$; the ammonia groups are co-ordinated with the zinc atoms. Similarly, the nickel salt is now found to have the formula

$$[Mo(SCN)_6(OH)]_2Ni_3(NH_3)_{17},2H_2O.$$

The corresponding *cadmium* salt, $[Mo(SCN)_6(OH)]_2Cd_3(NH_3)_{13}$, forms yellow crystals. A crystalline *salt*, $[Mo(SCN)_6(OH)]HCd,2H_2O$, is formed as a red precipitate on addition of cadmium sulphate to a concentrated aqueous solution of the *additive* compound of the ammonium salt and acetic acid, whilst in the presence of sulphuric acid the *precipitate* has the composition

$$[Mo(SCN)_6(OH)]Cd(NH_4),3H_2O.$$

A complex *salt*, $[Mo(SCN)_6(OH)]_2Cd_3,[Mo(SCN)_6(OH)]CdK,18H_2O$, is formed from the acetate of the potassium series. G. Y.

Fixation of Amines on the Ethylenic Linking of Alkyl Vinyl Ketones. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 543—551).—A more detailed account is given of the substances obtained by the addition of primary or secondary amines to alkyl vinyl ketones (Abstr., 1906, i, 142; 1907, i, 241).

Ethyl β-diethylaminoethyl ketone, $NEt_2\cdot CH_2\cdot CH_2\cdot COEt$, obtained by simple addition of diethylamine to ethyl vinyl ketone dissolved in ether, is a liquid of feebly basic odour and is readily soluble in water. The *semicarbazone*, m. p. 100°, and the *picrate*, m. p. 78°, are crystalline. On reduction, the amino-ketone furnishes the corresponding *amino-alcohol*, b. p. 80°/8 mm., which is liquid, has a feebly basic odour, and furnishes a *benzoate hydrochloride*, m. p. 75°, and a *phenylurethane hydrochloride*, m. p. 134°, both of which are crystalline.

Ethyl β-piperidinoethyl ketone, $C_5H_{10}N\cdot CH_2\cdot CH_2\cdot COEt$, b. p. 100°/7 mm., is liquid, possesses a piperidine-like odour, is slightly soluble in water, and yields a crystalline *semicarbazone*, m. p. 146°, *picrate*, m. p. 97°, *platinichloride*, m. p. 135° (approx.), and *oxime*, m. p. 50°. The oxime, on reduction by sodium amalgam in acetic acid, yields 1-γ-*aminoamylpiperidine*, $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot CHEt\cdot NH_2$, b. p. 100°/9 mm., which is liquid, has a strongly basic odour, is soluble in water, and furnishes a *hydrochloride*, m. p. 212° (approx.), *picrate*, m. p. 167°, and a *monohydrated platinichloride*, m. p. 216° (approx.), all of which are well crystallised. With potassium cyanate, the diamine yields the corresponding *carbamide*, m. p. 145°, which separates from benzene in colourless crystals, and with phenylcarbimide the corresponding *phenylcarbamide*, m. p. 104°, crystallising from benzene on addition of light petroleum. The diamine reacts with ethyl oxalate to form the corresponding *oxamide*, m. p. 128°, which crystallises from boiling acetic acid.

The interaction of primary amines and alkyl vinyl ketones is less simple than is that of the *sec.*-amines, since the former can react (1) with the ketone group, or (2) may simply add on to the ethylenic linking, forming a secondary amine, which may in its turn react with a second molecule of the alkyl vinyl ketone. The simple additive reaction is the principal one which occurs in presence of acetic or formic acid.

Ethyl β-propylaminoethyl ketone, $NHPr^a\cdot CH_2\cdot CH_2\cdot COEt$, b. p. 85°/12 mm., the chief product of the action of propylamine on ethyl vinyl ketone in presence of formic acid, is an unstable liquid of basic odour, and furnishes a *phenylcarbamide*, m. p. 115°, which separates from alcohol in brilliant lamellæ. In addition to the amino-ketone, a viscous *liquid* boiling at 156°/12 mm. is obtained in the above reaction, which may be the product of the further action of ethyl β-propylaminoethyl ketone on ethyl vinyl ketone, and has the constitution $COEt\cdot CH_2\cdot CH_2,NPr^a\cdot CH_2\cdot CH_2\cdot COEt$, but no definite semicarbazone could be obtained from it. The interaction of ammonia and ethyl vinyl ketone seems to be very complex, and no definite product could be isolated. T. A. H.

"Neuronal" (Bromodiethylacetamide). CARL MANNICH and F. ZERNIK (*Arch. Pharm.*, 1908, **246**, 178—186).—A continuation of work undertaken with a view to the determination of the constitution of neuronal. The results now recorded confirm the constitution previously suggested for the drug by Zernik (*Apoth. Zeit.*, 1904, 88).

When neuronal, $CEt_2Br\cdot CO\cdot NH_2$, is boiled with a solution of sodium hydroxide in water, it decomposes in two ways, yielding in the one case diethyl ketone with hydrobromic and hydrocyanic acids, and in the other, diethylglycollamide, $OH\cdot CEt_2\cdot CO\cdot NH_2$, and hydrobromic acid. *Diethylglycollamide*, m. p. 85—86°, crystallises in colourless leaflets from benzene, dissolves moist mercuric oxide on warming, is not attacked by alkaline permanganate, and yields neither diethyl ketone nor hydrogen cyanide when heated with alkali hydroxides, so that it is not an intermediate product in the first reaction. Neuronal dissolved in ether is decomposed by metallic sodium, yielding diethylcarbinol and hydrobromic and hydrocyanic acids. When boiled with water, neuronal loses 1 mol. of hydrogen bromide and furnishes *α-ethylcrotonamide*, $CHMe\colon CEt\cdot CO\cdot NH_2$, m. p. 99°, which crystallises in colourless needles, is readily soluble in alcohol or ether, slightly so in light petroleum, is not hydrolysed by alkalis, but is slowly attacked by boiling dilute sulphuric acid, forming ammonia and an indefinite oily product. It forms a *dibromide*, m. p. 128°, which crystallises from alcohol in colourless needles, and is readily soluble in chloroform or alcohol, but scarcely so in water. None of the three new substances described is physiologically active. T. A. H.

Preparation of α-Chloro*iso*valerylcarbamide. KNOLL & Co. (D.R.-P. 191386. Compare Abstr., 1907, i, 1017).—α-Chloro*iso*valeryl chloride and the corresponding bromide, prepared from α-chloro*iso*valeric acid and phosphoryl chloride and phosphorus tribromide respectively, react with carbamide, giving rise to α-chloro*iso*valerylcarbamide, m. p. 139°, a substance having marked hypnotic properties.
G. T. M.

Double Compounds of Hydrogen Peroxide with Organic Compounds. SIMEON M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 376—380).—Like inorganic compounds (compare Tanatar, Abstr., 1902, ii, 11; Willstätter, Abstr., 1903, ii, 537), a large number of organic compounds combine with hydrogen peroxide, forming compounds similar to those containing water of crystallisation. In certain cases, compounds which do not crystallise with water of crystallisation form crystalline compounds with hydrogen peroxide. The following compounds were prepared by evaporating, either on the water-bath or in a desiccator, solutions of the various substances in more or less concentrated hydrogen peroxide solutions.

Carbamide forms the moderately stable *compound*, $CO(NH_2)_2,H_2O_2$, which is deposited in large, transparent crystals, resembling those of potassium nitrate, and retains more than 15% (instead of 36·15%) of hydrogen peroxide after six months. Acetamide and urethane also unite with hydrogen peroxide, but no definite compounds could be obtained. Succinimide yields the *compound*, $C_4H_5O_2N,H_2O_2$, which is appreciably less stable than that formed by carbamide. Asparagine gives the viscous *compound*, $C_4H_8O_3N_2,H_2O_2$; mannitol, the moderately unstable *compound*, $C_6H_{14}O_6,H_2O_2$, and pinacone, the syrupy *compound*, $C_6H_{14}O_2,H_2O_2$, which evaporates completely on the water-bath and gives a distillate containing 8·93%, instead of 22·36%, of hydrogen peroxide. Erythritol forms an unstable, crystalline compound. Sucrose does not combine with hydrogen peroxide, whilst parabanic acid and ammonium oxalate yield crystalline compounds of indefinite composition.
T. H. P.

Synthesis of Ammonia and of Hydrogen Cyanide. HERMAN C. WOLTERECK (*Compt. rend.*, 1908, **146**, 929—931. Compare Abstr., 1904, ii, 115; this vol., ii, 174).—When heated moist air is blown through an apparatus containing incandescent charcoal, the escaping gases contain hydrogen cyanide and ammonia in quantities increasing with the temperature of the air and of the charcoal. If instead of air a mixture of air and ammonia is employed, hydrogen cyanide is also formed, together with ammonia, corresponding with an excess of 44% of the original quantity. The probable course of the reaction is the formation of hydrogen cyanide in the zone of highest temperature according to the equation $2N + O + H_2O + 4C = 2HCN + 2CO$, and the subsequent decomposition of part of the hydrogen cyanide to form ammonia and carbon monoxide, $HCN + H_2O \rightleftarrows NH_3 + CO$.

In one experiment of an hour's duration, 97·70 grams of hydrogen cyanide and 71·53 grams of ammonia were obtained by passing 820 kilos. of air at 300° over heated charcoal at 1260—1340°.
M. A. W.

Preparation of Dimethylglyoxime. A. GANDARIN (*J. pr. Chem.*, 1908, [ii], **77**, 414—416).—Since dimethylglyoxime has become of importance as a reagent for nickel and cobalt (Kraut, Abstr., 1906, ii, 858; Brunck, Abstr., 1907, ii, 582; Tschugaeff, *ibid.*, 989), an easy and cheap method of preparation was highly desirable. Such a method is now described. Methyl ethyl ketone is shaken with amyl nitrite and hydrochloric acid, D 1·19, at 40—50°; the product is treated with ice and sodium hydroxide, and the resulting alkaline solution of the *iso*nitroso-compound is heated with hydroxylamine hydrochloride. The reaction takes place according to the equations:
$C_2H_5\cdot COMe + HNO_2 = OH\cdot N\colon CMe\cdot COMe + H_2O$ and
$OH\cdot N\colon CMe\cdot COMe + NH_2\cdot OH = OH\cdot N\colon CMe\cdot CMe\colon N\cdot OH + H_2O$.

The pure dioxime is obtained in a yield of 650—700 grams from 850 c.c. of the ketone. The original should be consulted for details of the process. G. Y.

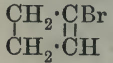
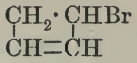
Synthesis by means of Organo-metallic Compounds. JOSEPH ZELTNER (*J. pr. Chem.*, 1908, [ii], **77**, 393—402; *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 381—391).—A résumé of the work of various authors on organo-metallic compounds. The capacity to form such compounds, which commences with the metals of the first group of the periodic system, reaches its maximum in the metals of the second group, and diminishes in the metals of groups III, IV, and V. The elements of groups VI and VII show no tendency to form organo-metallic compounds, but this tendency reappears in the transition group VIII. The stability of organo-metallic compounds of metals of the same group increases with the atomic weight of the metal and with the size of the organic radicle. If a reaction takes place in several stages, and it is desired to obtain the product of the first stage, it is advantageous to employ zinc rather than magnesium; conversely, if the final product is desired, or the reaction takes place in one stage, magnesium is to be preferred to zinc. The influence of the weight of the alkyl groups is seen in the formation of primary in place of secondary, and of secondary in place of tertiary, alcohols from zinc dipropyl and zinc compounds of higher alkyls (compare Bogomoletz, Abstr., 1881, 401). G. Y.

***cyclo*Octane and *cyclo*Heptane.** RICHARD WILLSTÄTTER and TOKUHEI KAMETAKA (*Ber.*, 1908, **41**, 1480—1486).—Willstätter and Bruce found that *cyclo*butane is reduced to butane by Sabatier and Senderens' method at 180—200° (Abstr., 1907, i, 1018), and that (*loc. cit.*) the reduction of *cyclo*propane to propane takes place still more easily at 80—120°. Sabatier and Senderens, on the other hand, have shown that *cyclo*hexane, when heated with nickel and hydrogen, does not form hexane, but at 270—280° decomposes, yielding methane and benzene. The behaviour of *cyclo*heptane and *cyclo*octane under similar conditions has now been studied.

When reduced with hydrogen and nickel at 235°, *cyclo*heptane is converted chiefly into methyl*cyclo*hexane, at the same time forming small amounts of dimethyl*cyclo*pentane. If the reduction is carried out at 250°, the product contains traces of aromatic hydrocarbon in consequence of the decomposition of methyl*cyclo*hexane, which commences at 240° (Sabatier and Senderens, Abstr., 1905, i, 401).

*cyclo*Octane, prepared by Willstätter and Veraguth's method (Abstr., 1907, i, 303), is obtained in a series of fractions: b. p. 142—144°/737 mm.; b. p. 144—147°/737 mm.; and m. p. 5—6°, b. p. 147·2—148·8°/737 mm. The first two fractions, when oxidised by nitric acid, yield suberic acid and a more easily soluble acid, m. p. 82—85°, which may be β-methyladipic acid. The fraction with the highest boiling point is probably pure *cyclo*octane. When reduced with nickel and hydrogen at 205—210°, it yields a product consisting chiefly of dimethyl*cyclo*hexane, together with, perhaps, alkylated *cyclo*pentanes.

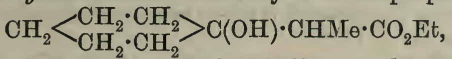
dicyclo*Octane*, C_8H_{14}, prepared by reduction of *dicyclo*octene (Willstätter and Veraguth, *loc. cit.*) by Sabatier and Senderens' method at 145—150°, has b. p. 139·5—140·5° (corr.), D_4^0 0·8775, D_4^{20} 0·8604, n_D^{20} 1·46148, is stable towards permanganate, and is coloured by bromine in traces. On reduction with hydrogen and nickel at 200—205°, *dicyclo*octane yields a mixture of hydrocarbons identical with the product obtained from *cyclo*octane, which may be formed intermediately. G. Y.

Constitution of *cyclo*Butene. RICHARD WILLSTÄTTER and JAMES BRUCE (*Ber.*, 1908, 41, 1486—1488. Compare Abstr., 1907, i, 1018; Willstätter and Schmaedel, Abstr., 1905, i, 514).—Zelinsky and Gutt's suggestion that *cyclo*butene has a dicyclic structure (this vol., i, 14) is discussed and rejected. The formation of *cyclo*butene from trimethyl*cyclo*butylammonium hydroxide and by the action of zinc on *cyclo*butene dibromide are in agreement with the monocyclic structure. *cyclo*Butene decolorises permanganate instantaneously, and forms an *additive* compound with bromine at –20°, whereas dicyclic hydrocarbons are stable towards these reagents. *cyclo*Butene dibromide is a 1 : 2-dibromide and not a 1 : 3-dibromide, as only 1 mol. of hydrogen bromide can be split off; the resulting bromo*cyclo*butene on oxidation yields succinic acid, and has therefore the constitution  $\begin{array}{l}CH_2\cdot CBr\\ \,|\qquad\ \ \|\\ CH_2\cdot CH\end{array}$, and not  $\begin{array}{l}CH_2\cdot CHBr\\ \,|\qquad\ |\\ CH{=}CH\end{array}$, as would be the case if *cyclo*butene had a dicyclic structure. G. Y.

Terpenes and Ethereal Oils. XCII. Preparation of Cyclic Hydrocarbons with Semicyclic Linkings and their Use in New Syntheses. OTTO WALLACH (*Annalen*, 1908, 360, 26—81).—As has been shown previously, the unsaturated hydrocarbons, formed by loss of water from tertiary alcohols, $(CH_2)_x{<}{\substack{CH_2\\CH_2}}{>}CR\cdot OH$, which are prepared from cyclic ketones by Grignard's reaction, usually have the ethylene linking in the cyclic nucleus. If, on the other hand, the cyclic ketone is condensed with ethyl bromoacetate and zinc, the resulting hydroxy-esters, $(CH_2)_x{<}{\substack{CH_2\\CH_2}}{>}C(OH)\cdot CH_2\cdot CO_2Et$, when treated with potassium hydrogen sulphate, yield unsaturated acids of the type $(CH_2)_x{<}{\substack{CH_2\\CH_2}}{>}C{:}CH\cdot CO_2H$, which on distillation form unsaturated hydrocarbons with semicyclic ethylene linkings,

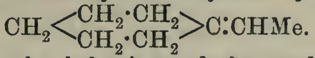
$$(CH_2)_x{<}{\substack{CH_2\\CH_2}}{>}C{:}CH_2.$$

Such hydrocarbons have been obtained also on distillation of unsaturated acids having an ethylene linking in the cyclic nucleus, molecular transformation taking place along with the loss of carbon dioxide. It is now found that unsaturated hydrocarbons with semicyclic ethylene linkings are obtained also from acids having the carboxyl group situated in a longer side-chain. Thus the condensation product of *cyclo*hexanone with ethyl α-bromopropionate,



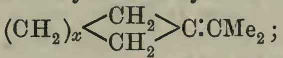
$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C(OH)\cdot CHMe\cdot CO_2Et},$$

on hydrolysis and distillation yields ethylidene*cyclo*hexane,



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C{:}CHMe}.$$

Of special interest is the behaviour of the condensation products of ethyl α-bromo*iso*butyrate, $\mathrm{(CH_2)}_x{<}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{C(OH)\cdot CMe_2\cdot CO_2Et}$. The removal of water from such substances can lead to the formation only of unsaturated esters containing a nucleus ethylene linking, $\mathrm{(CH_2)}_x{<}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH}\end{matrix}{\geqslant}\mathrm{C\cdot CMe_2\cdot CO_2Et}$. The corresponding acids on distillation lose carbon dioxide and yield the hydrocarbons,



$$\mathrm{(CH_2)}_x{<}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{C{:}CMe_2};$$

in this case, also, the ethylene linking wanders to the side-chain. In this manner, *o*-, *m*-, and *p*-menthenes with semicyclic ethylene linkings have been synthesised from the corresponding methyl*cyclo*hexanones.

The reverse transmigration of an ethylene linking from the semicyclic position into the nucleus has been observed previously as taking place under the influence of boiling mineral acids in the case of *p*-menthene (Abstr., 1906, i, 682) and of *iso*propylidenepentane (Abstr., 1907, i, 616). This is now found to be a general reaction, the ethylene linking being stable in the nucleus in aqueous acid solution, but in the semicyclic position in the absence of water and at high temperatures.

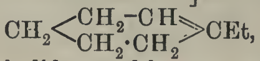
I. *Condensation of* cyclo*Hexanone with Ethyl α-Bromopropionate.*—[With Edgar Evans.]—*Ethyl* cyclo*hexanol*-1-*α-propionate*,

$$\mathrm{OH\cdot C_6H_{10}\cdot CHMe\cdot CO_2Et},$$

prepared in the usual manner from *cyclo*hexanone and ethyl α-bromopropionate, has b. p. 125—127°/12 mm. or 135—136°/20 mm., and when heated with potassium hydrogen sulphate at 150° yields the unsaturated *ester*, b. p. 108—112°/12 mm. This on hydrolysis forms cyclo*hexene-α-propionic acid*, b. p. 148—150°/13 mm.; the silver salt, $\mathrm{C_9H_{13}O_2Ag}$, was analysed. On distillation under the ordinary pressure, the acid yields cyclo*hexene-ethane* (*ethylidene*cyclo*hexane*), $\mathrm{C_6H_{10}{:}CHMe}$, b. p. 137—138°, D^{20} 0·8220—0·8225, n_D^{20} 1·4626—1·4631. This hydrocarbon readily forms a *nitrosochloride* in an 88% yield. The *nitrolpiperidide*, $\mathrm{C_5H_{10}N\cdot C_6H_{10}\cdot CMe{:}N\cdot OH}$, has m. p. 116—117°. The *methoxyloxime*, $\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{OMe}\\ \mathrm{CMe{:}N\cdot OH}\end{matrix}$, m. p. 85—86°, is formed from the nitrosochloride by the action of sodium methoxide. When heated successively with dimethylaniline and sulphuric acid, the nitrosochloride yields a mixture of acetophenone and cyclo*hexenyl methyl ketone*, $\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{\geqslant}\mathrm{C\cdot COMe}$. This is obtained by heating the nitrosochloride with sodium acetate and acetic acid, and distilling the product with steam in presence of sulphuric acid; it has b. p. 201—202°, D 0·9655, n_D^{20} 1·4881. The *semicarbazone*,

$C_9H_{15}ON_3$, m. p. 220—221°; the *oxime*, m. p. 99°. When reduced with sodium in alcoholic solution, the tetrahydro-ketone yields hexahydroacetophenone (*cyclo*hexyl methyl ketone), which forms a p-*nitrophenylhydrazone*, m. p. 154°.

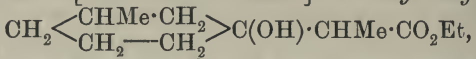
[With Paul Mendelsohn-Bartholdy.]—Ethyl-Δ^1-*cyclo*hexene,



$$CH_2<\begin{matrix}CH_2-CH\\CH_2\cdot CH_2\end{matrix}\geqslant CEt,$$

prepared by boiling ethylidene*cyclo*hexane with alcoholic sulphuric acid, is identical with Sabatier and Mailhe's hydrocarbon (Abstr., 1904, i, 666). It has b. p. 134—136°, D^{19} 0·8235, and n_D 1·4591. It forms a *nitrosochloride* readily, but in smaller yield than its isomeride. The *nitrolpiperidide*, m. p. 149°. When heated with sodium acetate and glacial acetic acid, the nitrosochloride yields a *ketone*, b. p. 195—200°, which has an odour resembling *cyclo*hexanone, and forms an *oxime*, m. p. 57°, and a *semicarbazone*, m. p. 175°.

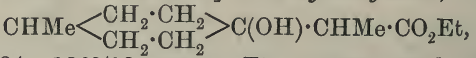
II. *Condensation of Active* 1-*Methyl*cyclo*hexane*-3-*one with Ethyl* α-*Bromopropionate*.—[With Edgar Evans.]—The *hydroxy*-ester,



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>C(OH)\cdot CHMe\cdot CO_2Et,$$

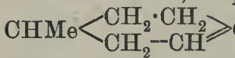
prepared in the usual manner from 1-methyl*cyclo*hexane-3-one, ethyl α-bromopropionate, and zinc, has b. p. 133—135°/13 mm. The unsaturated *ester*, b. p. 115—117°/13 mm. The unsaturated *acid*, b. p. 155—157°/17 mm., forms a *silver* salt, $C_{10}H_{15}O_2Ag$, and on distillation yields 1-*methyl*-3-*ethylidene*cyclo*hexane*, $C_6H_9Me\colon CHMe$, which has b. p. 153°, D 0·813, n_D 1·4584, and is lævorotatory. The *nitrosochloride* forms a *nitrolpiperidide*, m. p. 100—101°.

III. *Condensation of* 1-*Methyl*cyclo*hexane*-4-*one with Ethyl* α-*Bromopropionate*.—[With Edgar Evans.]—The *hydroxy*-ester,



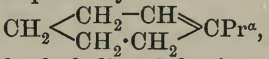
$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CHMe\cdot CO_2Et,$$

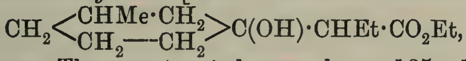
has b. p. 134—136°/13 mm. The unsaturated *ester*, b. p. 114—116°/13 mm. The unsaturated *acid*, b. p. 152—154°/13 mm., forms a *silver* salt, $C_{10}H_{15}O_2Ag$.

1-*Methyl*-4-*ethylidene*cyclo*hexane*, $C_{19}H_{16}$, has b. p. 156°, D^{20} 0·811, n_D^{20} 1·4571. The *nitrosochloride*, formed in an 83% to 85% yield, was converted into (*a*) the *nitrolpiperidide*, $C_{14}H_{26}ON_2$, which is obtained in two fractions, m. p. 127—128° and 133—134°, and (*b*) the *oxime*,  $CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2-CH\end{matrix}\geqslant C\cdot CMe\colon NOH$, m. p. 117°, which on hydrolysis is converted into 4-*acetyl*-1-*methyl*-Δ^1-cyclo*hexene*, $C_6H_8Me\cdot COMe$, b. p. 212—214°, D^{20} 0·942, n_D^{20} 1·4782. This forms a semicarbazone, $C_{10}H_{17}ON_3$, m. p. 220°. On reduction with sodium and alcohol, the tetrahydro-ketone is converted into a saturated *ketone*, which on treatment with hypobromite yields bromoform and an acid having the composition of hexahydrotoluic acid.

IV. *Condensation of* cyclo*Hexanone with Ethyl* α-*Bromo*-n-*butyrate*.—[With J. B. Churchill and Mahlon Rentschler.]—The *hydroxy*-ester, $OH\cdot C_6H_{10}\cdot CHEt\cdot CO_2Et$, has b. p. 145—150°/16 mm. The unsaturated *ester*, b. p. 122—127°/14 mm. The unsaturated *acid*, b. p. about 150°, forms a *silver* salt, $C_{10}H_{15}O_2Ag$; this acid reacts with hydrogen bromide in glacial acetic acid solution, forming a *bromo-acid*, $C_{10}H_{17}O_2Br$, m. p. 107—108°.

Propylidenecyclohexane, $C_6H_{10}\colon CHEt$, formed by distillation of the preceding unsaturated acid, has b. p. 157—158°, D 0·8210, n_D^{19} 1·4631. The *nitrosochloride*, $(C_9H_{16}ONCl)_2$, crystallises from benzene in prisms, m. p. 119°; the *nitrolpiperidide*, $C_5H_{10}N\cdot C_6H_{10}\cdot CEt\colon NOH$, m. p. 123°; the *methoxyl-oxime*, $OMe\cdot C_6H_{10}\cdot CEt\colon NOH$, m. p. 100—101°. Δ^1-cyclo*Hexenyl methyl ketone*, $C_6H_9\cdot COEt$, prepared by the action of dimethylaniline or of sodium acetate and hydrogen chloride in glacial acetic acid solution on the nitrosochloride, has b. p. 218°; the *semicarbazones*, obtained by the two methods of preparation, have m. p. 160—170° and 179—180° respectively.

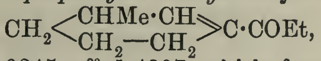
n-Propyl-Δ^1-*cyclo*hexene,  $CH_2{<}^{CH_2-CH}_{CH_2\cdot CH_2}{>}CPr^{\alpha}$, prepared by boiling propylidene*cyclo*hexane with alcoholic sulphuric acid, is identical with the hydrocarbon prepared by Sabatier and Mailhe's method (*loc. cit.*). It has b. p. 154—156°. The *nitrosochloride*, m. p. 104°; the *nitrolpiperidide*, m. p. 126—128°. The action of sodium methoxide on the *nitrosochloride* leads to the formation of an *oxime*; the corresponding *semicarbazone* has m. p. 140—141°.

V. *Condensation of Active* 1-*Methyl*cyclo*hexane*-3-*one with Ethyl a-Bromo*-n-*butyrate*.—[With MAHLON RENTSCHLER.]—The *hydroxy-ester*,  $CH_2{<}^{CHMe\cdot CH_2}_{CH_2-CH_2}{>}C(OH)\cdot CHEt\cdot CO_2Et$, has b. p. 165—170°/15 mm. The unsaturated *ester*, b. p. 135—140°/13 mm. The unsaturated acid forms a *silver* salt, $C_{11}H_{17}O_2Ag$. 1-*Methyl*-3-*propylidene*cyclo*hexane*, $C_{10}H_{18}$, b. p. 170—173°, D 0·814, n_D^{19} 1·4591, has a_D −32°3′ to 34°28′ (100 mm. tube). The *nitrolpiperidide*,

$$C_{10}H_7(NOH)\cdot C_5H_{10}N,$$

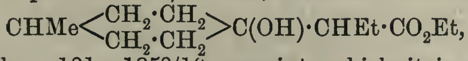
m. p. 96°. When heated with dimethylaniline and distilled with sulphuric acid, the nitrosochloride yields a ketone, which is obtained in two fractions: the fraction b. p. 218—220° forms a *semicarbazone*, m. p. 174°, whilst that of b. p. 225—228° forms a *semicarbazone*, m. p. 180°. On treatment of the ketone with 1% permanganate solution, a residue equal to about 40% of the whole and consisting of m-*tolyl ethyl ketone* was obtained. This forms a *semicarbazone*, $C_{11}H_{15}ON_3$, m. p. 175—176°, and an *oxime*, $C_{10}H_{13}ON$, m. p. 68—69°, and on oxidation with hypobromite solution yields *m*-toluic acid.

When heated with sodium acetate and glacial acetic acid, the nitrosochloride yields 3-*propionyl*-1-*methyl*-Δ^2-cyclo*hexene*,



$$CH_2{<}^{CHMe\cdot CH}_{CH_2-CH_2}{>}C\cdot COEt,$$

b. p. 220—222°, D 0·9345, n_D^{20} 1·4807, which forms a *semicarbazone*, $C_{11}H_{19}ON_3$, m. p. 193—194°.

VI. *Condensation of* 1-*Methyl*cyclo*hexane*-4-*one with Ethyl a-Bromo*-n-*butyrate*.—[With MAHLON RENTSCHLER.]—The condensation product, b. p. 138—140°/10 mm., consisted of a mixture of the *hydroxy*-ester,  $CHMe{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}C(OH)\cdot CHEt\cdot CO_2Et$, and the unsaturated *ester*, b. p. 121—125°/10 mm., into which it is converted completely by the action of potassium hydrogen sulphate. The *hydroxy-acid*,

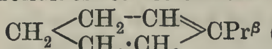
$$C_{10}H_{18}(OH)\cdot CO_2H,$$

m. p. 100—101°. The unsaturated *acid*, b. p. 154—158°/10 mm., forms a *silver* salt, $C_{11}H_{17}O_2Ag$.

The product, b. p. 175—177°, D^{19} 0·8135, n_D 1·4516, obtained on distilling the unsaturated acid, is a mixture consisting chiefly of 1-*methyl*-4-*propylidene*cyclo*hexane*, $C_6H_9Me\text{:}CHEt$, since on careful oxidation with permanganate it yields 1-methyl*cyclo*hexane-4-one and only traces of a keto-acid. The *nitrosochloride* was obtained in three fractions, m. p. 132—137°, 135—140°, and 138—141°, and the *nitrolpiperidide* in four fractions, m. p. 116—135°, 138—145°, 143—150°, and 150—152°. When treated with sodium acetate, the nitrosochloride forms an *oxime*, m. p. 105—106°, which yields an unsaturated *ketone*, m. p. 230—231°, D^{20} 0·952, n_D^{20} 1·4947; the *semicarbazone*, m. p. 183—184°. Reduction of the ketone leads to the formation of a saturated *ketone*, which forms a *semicarbazone*, $C_{11}H_{21}ON_3$, m. p. 178—179°, and on oxidation with hypobromite solution yields an acid. The *silver* salt, $C_8H_{13}O_2Ag$, was analysed.

After being boiled with alcoholic sulphuric acid, the methylpropylidene*cyclo*hexane, b. p. 175—177°, had b. p. 177—178°.

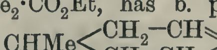
VII. *Condensation of* cyclo*Hexanone with Ethyl α-Bromo*iso*butyrate.*—[With HEINRICH MALLISON.]—The *hydroxy*-ester, b. p. 125—135°, on treatment with potassium hydrogen sulphate, yields the *acid*, $C_6H_9\cdot CMe_2\cdot CO_2Et$, which crystallises in rhombic prisms, m. p. 71—72°, b. p. 146—152°/13 mm., and on distillation forms iso*propylidene*cyclo*hexane*, $C_6H_{10}\text{:}CMe_2$. This solidifies in liquid air, has b. p. 160—161°, D^{20} 0·836, n_D^{20} 1·4723, and, on oxidation with permanganate, yields *cyclo*hexanone and a *glycol*, m. p. 82°. With nitrosyl chloride, *iso*propylidene*cyclo*hexane forms a blue oil, which solidifies to colourless crystals, m. p. 83°. *iso*Propyl-Δ¹-hexene,



$$CH_2{<}{}^{CH_2-CH}_{CH_2\cdot CH_2}{>}CPr^{\beta}$$

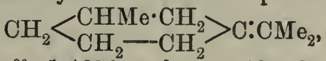
(Sabatier and Mailhe, *loc. cit.*), prepared by boiling the propylidene compound with alcoholic sulphuric acid, has b. p. 155—157°, D^{20} 0·829, n_D 1·4606. This hydrocarbon was obtained on one occasion by distillation of a crude specimen of the unsaturated acid. The *nitrosochloride* crystallises in white prisms, m. p. 129—130°, and when heated with alcoholic piperidine does not form a nitrolpiperidide, but yields an *oxime*, m. p. 72°, which is formed also by heating the nitrosochloride with sodium acetate and glacial acetic acid, and is hydrolysed by sulphuric acid to 1-iso*propylhexane*-2-*one*. This forms a *semicarbazone*, m. p. 165—166°.

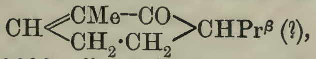
VIII. *Condensation of* 1-*Methyl*cyclo*hexane*-4-*one with Ethyl α-Bromo*iso*butyrate.*—[With J. B. CHURCHILL.]—The *hydroxy*-ester, $OH\cdot C_6H_9Me\cdot CMe_2\cdot CO_2Et$, has b. p. 148—150°/16 mm. The unsaturated *ester*,



$$CHMe{<}{}^{CH_2-CH}_{CH_2\cdot CH_2}{>}C\cdot CMe_2\cdot CO_2Et$$

b. p. 125—126°/13 mm., on hydrolysis yields 1-*methyl*-Δ³-cyclo*hexene*-4-α-iso*butyric acid*, m. p. 95—96°, together with small amounts of a crystalline *substance*, m. p. 194—195°. The unsaturated acid forms a *hydrobromide*, $C_{11}H_{19}O_2Br$, m. p. 112—117° if slowly, or 120—122° if quickly, heated. On distillation under the ordinary pressure, the unsaturated acid yields $\Delta^{4(8)}$-menthene (Abstr., 1906, i, 682), which on oxidation with permanganate at 0° yields acetone and 1-methyl*cyclo*hexane-4-one, together with β-adipic acid. *i*-Δ^3-Menthene, formed by boiling the semicyclic menthene with alcoholic sulphuric acid, can be converted by way of menthone into *i*-menthol, which is thus synthesised from 1-methyl*cyclo*hexane-4-one.

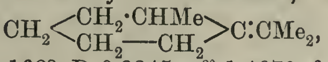
IX. *Condensation of* 1-*Methyl*cyclo*hexane*-3-*one with Ethyl Bromo*iso*butyrate.*—[With J. B. Churchill.]—1-*Methyl*cyclo*hexene*-3-iso*butyric acid,* b. p. 165—168°/14 mm., prepared by hydrolysis of its ester (Braun, Abstr., 1901, i, 157), forms a *hydrobromide*, $C_{11}H_{19}O_2Br$, m. p. 115—117°. The product obtained on distilling the unsaturated acid contains tetramethylsuccinic acid; hence Braun's ester must have contained ethyl tetramethylsuccinate, formed by the action of zinc on ethyl bromo*iso*butyrate. The chief product of the distillation is $\Delta^{3(8)}$-m-*menthene*,  $CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2\text{—}CH_2\end{matrix}>C{:}CMe_2$, which has b. p. 173—175°, D 0·8250, n_D^{20} 1·4670, when oxidised with permanganate yields 1-methyl*cyclo*hexane-3-one, and with nitrosyl chloride forms a blue *oil* volatile with steam. The semicyclic hydrocarbon is stable towards dilute aqueous sulphuric acid, but when boiled with alcoholic sulphuric acid is converted into a *hydrocarbon*, b. p. 164—168°, D 0·82, n_D 1·4561, which forms a solid *nitrosochloride.* Sodium methoxide converts this into an *oxime*; the corresponding *semicarbazone*, $C_{11}H_{19}ON_3$, m. p. 150—151°. Hydrolysis of the semicarbazone leads to the formation of *menthenone*,



$$CH\ll\begin{matrix}CMe\text{—}CO\\CH_2\cdot CH_2\end{matrix}>CHPr^{\beta}\ (?),$$

b. p. 208—209°, D 0·9202, n_D^{20} 1·4749, which when reduced with sodium and alcohol yields a m-*menthol*, $C_{10}H_{20}O_2$, b. p. about 215°, which has an odour of peppermint and is stable towards permanganate.

X. *Condensation of* 1-*Methyl*cyclo*hexane*-2-*one with Ethyl Bromo*iso*butyrate.*—[With J. B. Churchill.]—1-*Methyl*cyclo*hexene*-2-iso*butyric acid,* prepared by the usual series of reactions, has b. p. 162—164°/16 mm. The *silver* salt, $C_{11}H_{17}O_2Ag$, was analysed. When distilled, the unsaturated acid yields o-*menthene*,



$$CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2\text{—}CH_2\end{matrix}>C{:}CMe_2,$$

which has b. p. 160—162°, D 0·8345, n_D^{20} 1·4670, forms a blue *nitrosochloride*, and on oxidation with permanganate is converted into 1-methyl*cyclo*hexane-2-ol. When boiled with alcoholic sulphuric acid, the semicyclic *o*-menthene is transformed to only a small extent, as the product forms only traces of a solid *nitrosochloride.* G. Y.

Electrolysis of the Compounds of Aluminium Bromide with Toluene and Benzene. W. W. Neminsky and Wladimir A. Plotnikoff (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 391—396).—When the compounds, $AlBr_3,3C_6H_6$ and $AlBr_3,3C_7H_8$, described by Gustavson (Abstr., 1883, 577) are electrolysed with a platinised platinum cathode and a platinum or aluminium anode, benzene and toluene are liberated in amounts corresponding with three gram-mols. per 96·54 coulombs. The hydrocarbon collects mainly in the cathode compartment. The conductivity of the freshly-prepared complexes varies to some extent with the method of preparation and purification employed, and undergoes a gradual diminution. T. H. P.

Three Lecture Experiments on the Preparation of Iodochlorides and Iodoxy- and Iodonium Compounds. Conrad Willgerodt (*Ber.*, 1908, **41**, 1097—1098).—The formation of phenyliodochloride is strikingly shown by wetting the walls of a cylinder containing chlorine with a solution of iodobenzene in chloroform, when crystals of the compound are at once produced.

When the iodochloride is boiled with a freshly prepared solution of bleaching powder, iodoxybenzene separates after a short time in white crystals.

Diphenyliodonium chloride and iodide are readily prepared by adding hydrochloric acid or potassium iodide respectively to the corresponding iodonium hydroxide solution, itself prepared by rubbing sodium hydroxide and the iodochloride together until the solid disappears. W. R.

Studies in Nitration. II. Melting-Point Curves of Binary Mixtures of *o*-, *m*-, and *p*-Nitroanilines. A New Method for Determining the Composition of such Mixtures. J. Bishop Tingle and H. F. Roelker (*J. Amer. Chem. Soc.*, 1908, **30**, 822—828).—In an earlier paper (Tingle and Blanck, Abstr., 1907, i, 120), an account was given of the nitration of some *N*-substituted aniline derivatives. In the course of this investigation, a simple method was required for the determination of the composition of mixtures of the isomeric nitroanilines, and a study has therefore been made of the curves produced by plotting the melting points of binary mixtures of these substances against their composition.

In the case of the mixtures of *o*- and *m*-, and of *m*- and *p*-nitroanilines, these curves are comparatively regular; they fall to the eutectic point and then rise to the melting point of the pure compound. The curve for mixtures of *o*- and *p*-nitroanilines, however, is very irregular, and no explanation for this can at present be offered. The curves for the *o*- and *m*-, and *m*- and *p*-compounds can be employed for determining the composition of such mixtures by a simple and rapid method which requires very little material. The results are usually accurate within 2%. E. G.

Action of Sodium Hyposulphite on Nitro-derivatives. II. Alphonse Seyewetz and Noel (*Bull. Soc. chim.*, 1908, [iv], **3**, 497—500. Compare Seyewetz and Bloch, Abstr., 1906, i, 490).—It has been shown previously (*loc. cit.*) that, when nitro-derivatives of hydrocarbons are heated with sodium hyposulphite solution in presence of trisodium phosphate, there is a partial reduction of the nitro-group with the formation of sulphonamates of the type $R\cdot NH\cdot SO_3Na$. This reaction has now been extended to the dinitro-derivatives of aromatic hydrocarbons.

o-Dinitrobenzene is not readily attacked by the reagent, but yields a little *o*-phenylenediamine, and a small quantity of a product which appears to be sodium *o*-aminophenylsulphonamate. *m*-Dinitrobenzene furnishes in this reaction only *m*-phenylenediamine. 1-Chloro-2:4-dinitrobenzene furnishes 1% of *sodium chloroaminophenylsulphonamate*, m. p. 80—85°, which crystallises in colourless leaflets, is readily soluble in alcohol or water, but insoluble in ether or light petroleum. Sodium hyposulphite has no action under these conditions on dinitrotoluene or dinitronaphthalene. T. A. H.

Electrolytic Production of Nitrosobenzene. O. DIEFFENBACH (D.R.-P. 192519).—Although nitrosobenzene is the first product of the electrolytic reduction of nitrobenzene, it is not isolated in the ordinary method of effecting this reaction because of its conversion into azoxybenzene. It has now been found that when nitrobenzene is reduced in neutral electrolytes, nitrosobenzene is obtained in good yield. Two litres of 10% sodium sulphate and 150 grams of nitrobenzene were thoroughly stirred and electrolysed with 5 amperes for eight hours, the cathode being of nickel gauze, whilst the anode was of lead. On distillation, 35—40 grams of nitrosobenzene were obtained.

Other sulphates, such as those of magnesium or aluminium, may be used. An electrolytic cell with a diaphragm may be employed, and in this case the anode and cathode solutions are repeatedly changed during electrolysis, and care is taken that both solutions remain neutral. G. T. M.

Amides of *p*-Aminobenzenesulphonic Acid. P. GELMO (*J. pr. Chem.*, 1908, [ii], 77, 369—382).—The action of acetylaniline-*p*-sulphonyl chloride on ammonia and aromatic amines and the behaviour of the resulting acetylaniline-*p*-sulphonamides towards hydrolysing agents have been studied in extension of Schroeter's investigation of the acylanilinesulphonic acids and the action of acylanilinesulphonyl chlorides on diazo-salts (Abstr., 1906, i, 415).

Acetylaniline-*p*-sulphonyl chloride reacts with aqueous ammonia, aniline, and the toluidines, with development of heat, or with the naphthylamines in hot alcoholic solution, forming acetylaniline-*p*-sulphonamides, which crystallise in glistening leaflets, and are stable towards dilute ammonia, acids, or alkalis at the ordinary temperature, but are hydrolysed on prolonged boiling with dilute acids or alkalis, yielding the anilinesulphonamides, or by hot concentrated acids or alkalis, forming acetic and *p*-sulphanilic acids and the corresponding amines. The hydrolysis takes place most easily with acetylaniline-*p*-sulphonamide, least so with the acetylaniline-*p*-sulphon-naphthylamides. The aniline-*p*-sulphonamides crystallise in needles, yield crystalline *hydrochlorides* and, if derived from aromatic amines, nitroso-derivatives; they also form diazo-salts, from which azo-dyes are obtained resembling those, such as Orange II, prepared from sulphanilic acid.

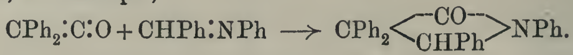
The following acetylaniline-*p*-sulphonamides, $NHAc\cdot C_6H_4\cdot SO_2\cdot NHR$, and aniline-*p*-sulphonamides, $NH_2\cdot C_6H_4\cdot SO_2\cdot NHR'$, are described; the temperatures are melting points:

$R = H$, 219°; $R' = H$, 163°; $R = Ph$, 214°; $R' = Ph$, 200°; $R = o\text{-}C_7H_7$, 236°; $R' = o\text{-}C_7H_7$, 132°; $R = m\text{-}C_7H_7$, 205°; $R' = m\text{-}C_7H_7$, 135°; $R = p\text{-}C_7H_7$, 209°; $R' = p\text{-}C_7H_7$, 109°; $R = \alpha\text{-}C_{10}H_7$, 215°; $R' = \alpha\text{-}C_{10}H_7$, 196°; $R = \beta\text{-}C_{10}H_7$, 212°; $R' = \beta\text{-}C_{10}H_7$, 203°. G. Y.

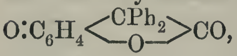
Some Derivatives of 2 : 6-Dinitro-1 : 3-dimethylbenzene-4-sulphonic Acid. William J. Karslake and W. J. Morgan (*J. Amer. Chem. Soc.*, 1908, 30, 828—831).—2 : 6-Dinitro-1 : 3-dimethylbenzene-4-sulphonyl chloride, m. p. 123°, was prepared by the action of phosphorus pentachloride on the potassium salt (Claus and Schmidt, Abstr., 1886, 708). The *anilide*, m. p. 154°, prepared by the action of the sulphonyl chloride on aniline, forms yellow needles. The o-*toluidide*, m. p. 135°, crystallises in white needles. By the action of the sulphonyl chloride on benzene in presence of aluminium chloride, 2 : 6-*dinitro*-1 : 3-*dimethylphenyl phenyl sulphone*, m. p. 178°, is produced, and forms large, lustrous plates. On oxidising potassium 2 : 6-dinitro-1 : 3-dimethylbenzene-4-sulphonate with potassium permanganate and treating the product with phosphorus pentachloride, a *substance*, m. p. 127—128°, was obtained, which was probably an impure acid chloride. By the action of ammonia on this compound, a substance was produced which crystallises in yellow plates, chars at about 290°, and is probably 2 : 4-*dinitro*-6-*sulpho*-m-*toluic acid*; its *barium*, *strontium*, and *barium hydrogen* salts are described. E. G.

Preparation of Pure Indene. Johannes Boes (*Chem. Zentr.*, 1908, i, 469; from *Apoth. Zeit.*, 1907, 22, 1137).—The isolation of indene from the nitrosite by treatment with water, dilute acids, dilute alkalis, or by dry distillation was unsuccessful. Reduction by means of zinc and hydrochloric acid yielded, instead of indene, a base apparently without aromatic character, which was volatile in steam, and gave a crystalline platinichloride and zincichloride. From the product obtained by heating a benzene solution of indene with metallic potassium or potassium hydroxide, only polymerised indene could be obtained. J. V. E.

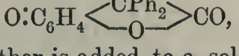
Ketens. VIII. Preparation of Quinonoid Hydrocarbons from Diphenylketen. Hermann Staudinger (*Ber.*, 1908, 41, 1355—1363. Compare this vol., i, 318).—Ketoketens are readily added on to some compounds containing the $\dot{}C{:}N-$ group, yielding β-lactams, for example,



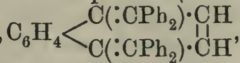
$$CPh_2{:}C{:}O + CHPh{:}NPh \longrightarrow CPh_2{<}\begin{smallmatrix}-CO-\\ CHPh\end{smallmatrix}{>}NPh.$$

Addition to a carbonyl group also occurs when an olefine double linking is adjacent to the carbonyl group, as, for instance, with quinone and dibenzylideneacetone. The β-lactones thus formed, such as  $O{:}C_6H_4{<}\begin{smallmatrix}CPh_2\\ -O-\end{smallmatrix}{>}CO$, are readily decomposed when heated, yielding compounds of the type of diphenylquinomethane and tetraphenylquinodimethane. The reaction appears to afford a fairly general method for transforming a reactive $\dot{}CO$ group into a $\dot{}C{:}CPh_2$ group.

Phenylcarbimide and phenylthiocarbimide do not form additive compounds with quinone in the same manner as diphenylketen.

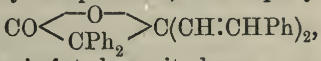
The *β-lactone*,  $O{:}C_6H_4{<}\begin{smallmatrix}CPh_2\\ -O-\end{smallmatrix}{>}CO$, separates when a suspension of quinone in dry ether is added to a solution of diphenylketen in light petroleum, and may be crystallised from hot benzene, ethyl acetate, or acetone. When heated it decomposes at 143°, carbon dioxide and quinone are evolved, and a reddish-brown mass is left. Diphenylquinomethane (Abstr., 1903, i, 639) is readily formed when the β-lactone is heated under reduced pressure, first at 100° and afterwards at 110°. Tetraphenylquinodimethane, $CPh_2:C_6H_4:CPh_2$ (Abstr., 1904, i, 491), is formed when the β-lactone is heated with xylene, but a better yield is obtained when a xylene solution of diphenylketen (2 mols.) (or diphenylketenquinoline) and quinone (1 mol.) is boiled.

Tetraphenylxyloquinodimethane, $CPh_2:C_6H_2Me_2:CPh_2$, is obtained from *p*-xyloquinone and diphenylketen. It crystallises from xylene in red needles with a purple lustre, and has m. p. 200° (decomp.).

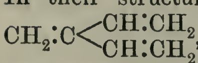
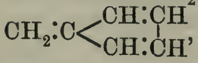
Tetraphenyl-α-naphthaquinodimethane,  $C_6H_4<\begin{array}{l}C(:CPh_2)\cdot CH\\ \qquad\qquad\quad \| \\ C(:CPh_2)\cdot CH\end{array}$, separates from benzene as a light yellow powder, m. p. 262—263°, but orange-coloured at about 200°.

When diphenylketenquinoline and anthraquinone are heated together at 190—200°, carbon dioxide is evolved, and a colourless product $C_{40}H_{28}$, m. p. 302—303°, is obtained. J. J. S.

New Method for Preparation of Homologues of Naphthalene. GEORGES DARZENS and H. ROST (*Compt. rend.*, 1908, **146**, 933—934).—Naphthyl alkyl ketones (Rosset, Abstr., 1897, i, 75; 1898, i, 593), like the phenyl alkyl ketones (Abstr., 1905, i, 66), are converted quantitatively into the corresponding hydrocarbon by direct hydrogenation at 180° in the presence of nickel, obtained by reducing the oxide at 250°. The following alkylnaphthalenes were thus prepared: α- and β-ethylnaphthalenes from α- and β-acetylnaphthalenes respectively; α-iso*butylnaphthalene*, b. p. 136—138°/11 mm., from α-*iso*butyrylnaphthalene, is a mobile liquid with an odour of petroleum; β-iso*butylnaphthalene*, b. p. 112—113°/6 mm., from β-*iso*butyrylnaphthalene, is a mobile liquid with a slight odour. M. A. W.

Ketens. IX. Coloured Hydrocarbons from Diphenylketen. HERMANN STAUDINGER (*Ber.*, 1908, **41**, 1493—1500).—It has been shown in the previous communication on this subject (this vol., i, 318) that only those carbonyl compounds which have a double linking in the neighbouring position react readily with ketoketens. In agreement with this, dibenzylideneacetone forms an *additive* compound with diphenylketen slowly at the ordinary temperature, but rapidly in boiling toluene solution. The β-lactone,  $CO<\begin{array}{c}-O-\\ CPh_2\end{array}>C(CH:CHPh)_2$, formed as the primary product cannot be isolated, as it decomposes even in the cold more rapidly than it is formed, yielding carbon dioxide and αε-diphenyl-γ-diphenylmethylene-$\Delta^{\alpha\delta}$-pentadiene,

$CPh_2:C(CH:CHPh)_2$.

In their structure, the derivatives of γ-methylene-$\Delta^{\alpha\delta}$-pentadiene,  $CH_2:C<\begin{array}{l}CH:CH_2\\ CH:CH_2\end{array}$, formed in this manner, resemble the fulvenes,  $CH_2:C<\begin{array}{l}CH:CH\\ \qquad\;\; | \\ CH:CH\end{array}$, and may be termed "acyclic fulvenes." Only one acyclic fulvene has been previously prepared (Fellenberg, Abstr., 1904, i, 961). It is a colourless substance, as is probably also the parent γ-methylene-$\Delta^{a\delta}$-pentadiene, colour appearing in this group only when the hydrogen atoms are substituted by phenyl groups; the acyclic fulvenes derived from diphenylketen are coloured, but less strongly than the fulvenes, which is in analogy to the fact that diphenylfulvene is much more strongly coloured than fulvene.

The acyclic fulvenes undergo auto-oxidation, but to a less degree than the fulvenes, whilst, in agreement with Thiele and Bühner's observation (Abstr., 1906, i, 569) that only hydrocarbons with a *cyclo*pentadiene grouping can be reduced by aluminium amalgam, the acyclic fulvenes are stable towards this reagent.

Di-*p*-chlorobenzylidene-, dianisylidene-, and dicinnamylidene-acetones react with diphenylketen in the same manner and under the same conditions as does dibenzylideneacetone; phorone and methyl and ethyl ketopentadienedicarboxylates, on the other hand, react with diphenylketen only at high temperatures and to a small extent. Those ketones which react readily with diphenylketen also form coloured *additive* compounds with hydrogen haloids (Baeyer and Villiger, Abstr., 1902, i, 1189; Baeyer, Abstr., 1905, i, 281), the capacities for the two reactions disappearing simultaneously. These facts are opposed to Vorländer and Mumme's view that the capacity of an ethylene linking for adding on hydrogen haloids is diminished by the proximity of a carbonyl group (Abstr., 1903, i, 495).

αε-Diphenyl-γ-diphenylmethylene-$\Delta^{a\delta}$*-pentadiene*, $C_{30}H_{24}$, prepared by boiling dibenzylideneacetone with diphenylketen in toluene solution, or by fusing dibenzylideneacetone with diphenylketenquinoline, crystallises from ethyl acetate in sulphur-yellow needles, m. p. 173—174°, or from benzene in yellow needles containing C_6H_6, which is lost at 130°. It is converted into resinous products when boiled in benzene in presence of air, and does not form *additive* compounds with hydrogen haloids, but yields a *tetrabromide*,

$$CPh_2{:}C(CHBr{\cdot}CHBrPh)_2,$$

which crystallises in colourless plates, m. p. 168·5—169°, and is stable to dry bromine in chloroform solution or to permanganate in acetone-benzene solution, but reacts readily with moist bromine, forming hydrogen bromide and benzaldehyde.

*αε-Di-*p*-methoxyphenyl-γ-diphenylmethylene-*$\Delta^{a\delta}$*-pentadiene*,

$$CPh_2{:}C(CH{:}CH{\cdot}C_6H_4{\cdot}OMe)_2,$$

prepared from dianisylideneacetone and diphenylketen or its quinoline additive compound, crystallises in yellow needles with green fluorescence, which become yellow at 130°, m. p. 176·5—177·5°.

*αε-Di-*p*-chlorophenyl-γ-diphenylmethylene-*$\Delta^{a\delta}$*-pentadiene*, $C_{30}H_{22}Cl_2$, m. p. 195·5—196·5°, crystallises from benzene.

αε-Distyryl-γ-diphenylmethylene-$\Delta^{a\delta}$*-pentadiene*,

$$CPh_2{:}C(CH{:}CH{\cdot}CH{:}CHPh)_2,$$

crystallises from benzene in yellow prisms ($\frac{1}{2}C_6H_6$), or from glacial acetic acid or ethyl acetate in yellow needles, m. p. 150—151°.

Diphenylketenquinoline reacts with methyl ketopentadienedicarboxylate at 140—150°, with the ethyl ester at 150—160°, and with phorone at 180—190°, yielding carbon dioxide; a crystalline product could not be obtained. G. Y.

Crystallography of some Cyclic Organic Compounds. Franz M. Jaeger (*Zeitsch. Kryst. Min.*, 1908, **44**, 561—575).—Crystallographic determinations are given of the following compounds: *o*-Nitrosoacetanilide, monoclinic $[a:b:c=0{\cdot}8940:1:0{\cdot}7295;\ \beta=97°54']$. *o*-Nitroacetanilide, monoclinic $[a:b:c=0{\cdot}8935:1:1{\cdot}9198;\ \beta=96°9']$. 2:4:6-Trichlorobenzamide, rhombic
$[a:b:c=0{\cdot}5380:1:1{\cdot}5180]$.
Lupeone, rhombic $[a:b:c=0{\cdot}8071:1:1{\cdot}2248]$. Cholestenone, monoclinic $[a:b:c=0{\cdot}8463:1:1{\cdot}3538;\ \beta=104°44']$. β-Phytosteryl acetate tetrabromide, monoclinic $[a:b:c=2{\cdot}4832:1:3{\cdot}7797;\ \beta=113°33\tfrac{1}{2}']$. 6-Hydroxy-2:4-dimethylpyrimidine $(+2H_2O)$, monoclinic $[a:b:c=0{\cdot}6815:1:1{\cdot}0142;\ \beta=101°9']$; its nitrate is triclinic $[a:b:c=0{\cdot}9323:1:0{\cdot}9951;\ \alpha=112°45\tfrac{1}{3}';\ \beta=95°4\tfrac{2}{3}';\ \gamma=78°5']$. *o*-Nitrobenzoylpiperidide, triclinic $[a:b:c=1{\cdot}3444:1:0{\cdot}9672;\ \alpha=101°34';\ \beta=95°59\tfrac{1}{3};\ \gamma=70°36']$. *p*-Nitrobenzoylpiperidide, rhombic $[a:b:c=1{\cdot}1128:1:0{\cdot}9620]$. Piperine, monoclinic $[a:b=0{\cdot}9837:1;\ \beta=109°37\tfrac{3}{4}']$. 1:3-Dichloro-4:5-dinitrobenzene, tetragonal
$[a:c=1:2{\cdot}0306]$. L. J. S.

Bromination. Julius B. Cohen and W. E. Cross (*Amer. Chem. J.*, 1908, **39**, 431—432). Solomon F. Acree, J. M. Johnson, and Sidney Nirdlinger (*ibid.*, 544—554).—Polemical. A question of priority (see Proc., 1907, **23**, 148; this vol., ii, 29).

Action of Sodium Hydroxide on Derivatives of Dithiodiglycollic Acid and Diselenodiglycollic Acid. Gustav Frerichs and Edwin Wildt (*Annalen*, 1908, **360**, 105—127).—As is well known, the action of sodium hydroxide on phenyl disulphide leads to the formation of thiophenol and benzenesulphonic acid. A similar, simultaneous reduction and oxidation is now found to take place with the arylamides of dithiodiglycollic acid; these yield the corresponding thioglycollamides and derivatives of thionoxalic acid, which appear instead of the sulphonic acid. Diselenodithioglycollamides, on the other hand, under the same conditions, yield derivatives of selenoxalic acid, but together with selenodiglycollamides instead of selenoglycollamides. Dithiodiglycollarylamides are prepared by the action of hydrogen peroxide on carbaminethioglycollarylamides in ammoniacal solution (Beckurts and Frerichs, Abstr., 1902, i, 763). The preparation of diselenodiglycollarylamides is described by Frerichs (Abstr., 1903, i, 609).

When moistened with alcohol and boiled for two to three minutes with 20% sodium hydroxide solution, dithiodiglycollanilide yields thioglycollanilide and thionoxanilide (Reissert, Abstr., 1904, i, 999), together with small amounts of hydrogen sulphide, phenylcarbimide, thionoxanilic acid, and aniline thionoxanilate (Reissert, *loc. cit.*), which are formed by decomposition of the thionoxanilide. When treated with hydrogen peroxide in sodium hydroxide solution, thionoxanilide yields oxanilide.

Thionoxal-p-*toluidide*, $C_6H_4Me{\cdot}NH{\cdot}CS{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$, formed together with thioglycoll-*p*-toluidide from dithiodiglycoll-*p*-toluidide, crystallises in yellow needles, m. p. 153—154°, and is oxidised to oxal-*p*-toluidide by the action of hydrogen peroxide in sodium hydroxide solution. *Thionoxal*-o-*toluidide*, crystallising in yellow leaflets or needles, m. p. 126°, and *thionoxal*-m-*toluidide*, crystallising in yellow needles or leaflets, m. p. 88—89°, were obtained in the same manner.

Carbaminethioglycoll-p-*chloroanilide*,

$$C_6H_4Cl\cdot NH\cdot CO\cdot CH_2\cdot S\cdot CO\cdot NH_2,$$

prepared by successive treatment of *p*-chloroaniline with chloroacetic acid and potassium thiocyanate, separates from alcohol in crystals, m. p. 174° (decomp.). *Dithiodiglycoll*-p-*chloroanilide*,

$$S_2(CH_2\cdot CO\cdot NH\cdot C_6H_4Cl)_2,$$

crystallises from alcohol in colourless needles, m. p. 194—195°. *Thionoxal*-p-*chloroanilide*, $C_6H_4Cl\cdot NH\cdot CS\cdot CO\cdot NH\cdot C_6H_4Cl$, forms long, yellow needles, m. p. 157—158°.

Carbaminethioglycoll-ψ-cumidide,

$$C_6H_2Me_3\cdot NH\cdot CO\cdot CH_2\cdot S\cdot CO\cdot NH_2,$$

prepared from ψ-cumidine, chloroacetic acid, and potassium thiocyanate, separates from alcohol in crystals, m. p. 171—172° (decomp.). *Dithiodiglycoll-ψ-cumidide*, $S_2(CH_2\cdot CO\cdot NH\cdot C_6H_2Me_3)_2$, separates from glacial acetic acid in crystals, m. p. 194—195°. *Thionoxal-ψ-cumidide*, $C_6H_2Me_3\cdot NH\cdot CS\cdot CO\cdot NH\cdot C_6H_2Me_3$, crystallises from alcohol in yellow needles, m. p. 179—180°.

Thionoxal-p-phenetidide,

$$OEt\cdot C_6H_4\cdot NH\cdot CS\cdot CO\cdot NH\cdot C_6H_4\cdot OEt,$$

is obtained in crystals, m. p. 156—157°.

The following naphthyl derivatives were prepared in the same manner:

Carbaminethioglycoll-α-naphthylamide, $C_{13}H_{12}O_2N_2S$, colourless needles, m. p. 165—166° (decomp.). *Dithiodiglycoll-α-naphthylamide*, $C_{24}H_{20}O_2N_2S_2$, m. p. 210—211°. *Thionoxal-α-naphthylamide*,

$$C_{22}H_{16}ON_2S,$$

yellow needles, m. p. 184—185°. *Carbaminethioglycoll-β-naphthylamide*, white needles, m. p. 185—186° (decomp.). *Dithiodiglycoll-β-naphthylamide*, white needles, m. p. 204—205°. *Thionoxal-β-naphthylamide*, yellow needles, m. p. 184—185°.

The following new selenocyanoacetamides,

$$NHR\cdot CO\cdot CH_2\cdot SeCN,$$

diselenodiglycollamides, $Se_2(CH_2\cdot CO\cdot NHR)_2$, selenodiglycollamides, $Se(CH_2\cdot CO\cdot NHR)_2$, and amides of selenoxalic acid,

$$NHR\cdot CSe\cdot CO\cdot NHR,$$

are described.

$R = Ph$: *selenodiglycollanilide*, white needles, m. p. 198°; *selenoxanilide*, red needles, m. p. 139·5—140·5°. $R = C_6H_4Me$: *selenodiglycoll*-p-*toluidide*, m. p. 217—218°; *selenoxal*-p-*toluidide*, red needles, m. p. 165—166°; *selenodiglycoll*-m-*toluidide*, white needles, m. p. 170—171°; *selenoxal*-m-*toluidide*, m. p. 73—74°; *selenoxal*-o-*toluidide*, red needles and leaflets, m. p. 131·5—132·5°. $R = C_6H_4Cl$: *diselenodiglycoll*-p-*chloroanilide*, yellow needles, m. p. 172—173°; *selenodiglycoll*-p-*chloroanilide*, m. p. 190—191°; *selenoxal*-p-*chloroanilide*, yellowish-red needles, m. p. 166°. $R = C_6H_4\cdot OMe$: *selenocyanoacet*-p-*phenetidide*, yellow needles, m. p. 162—163° (decomp.);

diselenodiglycoll-p-*phenetidide*, yellow needles, m. p. 161—162°; *selenodiglycoll*-p-*phenetidide*, m. p. 199—200°; *selenoxal*-p-*phenetidide*, red needles, m. p. 160—161°.

Selenodiglycollanilide, prepared by the action of chloroacetanilide on potassium selenide, is identical with that obtained by treating diselenodiglycollanilide with sodium hydroxide. G. Y.

9-Aminofluorene. JULIUS SCHMIDT and HERMANN STÜTZEL (*Ber.*, 1908, **41**, 1243—1252).—Schmidt and Mezger (Abstr., 1907, i, 43) have shown that the acetyl derivative of 9-hydroxyfluorene exists in two stereoisomeric modifications. 9-Aminofluorene studied from the same point of view is found to exist as an α-isomeride, m. p. 53—55°, and as a β-isomeride, m. p. about 123°; these form identical derivatives, excepting in the case of the compound formed with phenylcarbimide.

9-Aminofluorene has previously been described by Wegerhoff as having m. p. 50—60° (*Annalen*, 1889, **252**, 37), and by Kerp (Abstr., 1896, i, 239) as m. p. 161°.

On reducing fluorenoneoxime with zinc and acetic acid, a mixture of the two modifications is produced, m. p. 50—80°, which is separated by fractional crystallisation from light petroleum (b. p. 50—70°). The low melting α-9-aminofluorene separates first in splendid colourless needles, m. p. 53—55°, and dissolves in concentrated sulphuric acid with a green coloration. β-9-Aminofluorene crystallises in flocculent aggregates of minute needles, m. p. 123°, and on heating with solvents is slowly converted into the α-modification.

The following derivatives may be prepared from either isomeride. The *hydrochloride* forms colourless needles, sparingly soluble in water; the *nitrate* crystallises in needles, m. p. 180° (decomp.); the *picrate* forms yellow needles, which become brown at 180°, m. p. 240°; the *picrolonate*, $C_{13}H_{11}N\cdot C_{10}H_8O_5N_4$, separates in orange-yellow needles, which become green at 210°, m. p. 265° (decomp.). The *acetate* gives colourless needles, m. p. 260—261°; the *benzoate* forms colourless, silky, glistening needles, also m. p. 260—261°; indeed, these two compounds are remarkably alike. The *benzylidene* derivative forms yellow prisms, m. p. 141°.

9-*Fluorylcarbamide*, $C_{13}H_9\cdot NH\cdot CO\cdot NH_2$, yields colourless crystals, which do not melt at 300°. sym-*Di*-9-*fluorylthiocarbamide*,

$$CS(NH\cdot C_{13}H_9)_2,$$

prepared by heating aminofluorene with alcohol and carbon disulphide, forms colourless crystals, m. p. 243°, with possibly also an indication of a lower melting isomeride. sym-9-*Fluorylphenylcarbamide*, obtained from α-9-aminofluorene, has m. p. 310° (decomp.); prepared from the β-form, it has m. p. 340° (decomp.). E. F. A.

Formation of Carbodiphenylimide from Phenylcarbimide. ROBERT STOLLÉ (*Ber.*, 1908, **41**, 1125—1126. Compare Hofmann, Abstr., 1885, 774).—Phenylcarbimide is converted into carbodiphenylimide with the liberation of carbon dioxide when heated in sealed tubes at 180°. The same product is obtained when triphenyl*iso*cyanurate is heated at 300°. During the preparation of the latter compound from phenylcarbimide and potassium acetate, the formation of an *acid*, m. p. 220°, was observed, the investigation of which is in progress. W. H. G.

The Iodine Value of the Phenols. Ernest Wake and Harry Ingle (*J. Soc. Chem. Ind.*, 1908, **27**, 315—316).—The iodine values of certain phenols have been examined. *o*- and *p*-Polyphenols liberate iodine from Wys's solution, but not meta-derivatives, the reaction affording a test for the position of the hydroxyl group, and also for impurities in meta-compounds. α-Naphthol liberates iodine from Wys's solution, but β-naphthol does not. Free phenols absorb iodine in the ring, but phenolic esters (benzoates) do not.

The *product* of the action of Wys's solution on β-naphthol forms feathery, silky needles, m. p. 87°, which dissolve readily in alcohol, ether, and alkaline solutions. Analysis points to the formula $C_{10}H_7I(OH)_2$. A. J. W.

Preparation of Arylsulphonyl Derivatives of 1:2- and 2:1-Aminonaphtholsulphonic Acids. Actien Gesellschaft für Anilin-Fabrikation (D.R.-P. 193099).—The sulphonic acids of the 1 : 2- and 2 : 1-aminonaphthols, when treated with *p*-toluenesulphonyl chloride in alkaline solution, give a good yield (90—95%) of diazotisable *p*-toluenesulphonyl derivatives, which can be employed in the production of *o*-hydroxyazo-dyes.

The p-*toluenesulphonyl* derivative of 1-amino-β-naphthol-4-sulphonic acid is precipitated from alkaline solutions by acids, and melts indefinitely at 150—160°. G. T. M.

Condensation Products of Aliphatic Aldehydes with Phenol. A. I. Lunjak (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 466—470. Compare Abstr., 1904, i, 495).—The following further condensation products have been prepared.

Di-p-*hydroxydiphenylpropane*, $C_2H_5\cdot CH(C_6H_4\cdot OH)_2$, prepared from phenol and propaldehyde, crystallises from water in aggregates of needles, m. p. 130°. Its *dibenzoyl* derivative, $C_2H_5\cdot CH(C_6H_4\cdot OBz)_2$, is deposited from alcohol in crystals, m. p. 146°. Its *dimethyl ether*, $C_2H_5\cdot CH(C_6H_4\cdot OMe)_2$, crystallises from a mixture of ether and alcohol in rhombic plates, m. p. 44°, b. p. 362·5—364·5°/743·6 mm.; when oxidised with chromic acid, it yields di-*p*-methoxybenzophenone and anisic acid.

Di-p-*hydroxydiphenylbutane*, $C_4H_8(C_6H_4\cdot OH)_2$, prepared from phenol and *n*-butaldehyde, crystallises from water in long, silky needles, m. p. 136°. Its *dibenzoyl* derivative, $C_4H_8(C_6H_4\cdot OBz)_2$, separates from alcohol in crystals, m. p. 124°. Its *dimethyl ether*, $C_4H_8(C_6H_4\cdot OMe)_2$, has b. p. 228·8—229·3°/7 mm., D_0^0 1·0690, D_0^{20} 1·0563, D_{20}^{20} 1·0572, and yields di-*p*-methoxybenzophenone and anisic acid on oxidation with chromic acid. T. H. P.

[1 : 2′-Dihydroxy-1′ : 4′-dimethyldiphenylamine and its Indophenol Derivative.] Leopold Cassella & Co. (D.R.-P., 191863). —An alkaline solution of *p*-xylenol and *p*-aminophenol, when oxidised with sodium hypochlorite, furnishes the sodium salt of *indophenol*, which, when liberated with acid dissolved in hot dilute alcohol, separates on cooling in red crystals, m. p. 154°. 1 : 2′-*Dihydroxy*-1′ : 4′-*dimethyldiphenylamine*, $HO\cdot C_6H_4\cdot NH\cdot C_6H_2Me_2\cdot OH$, colourless, m. p. 158°, is obtained from the indophenol by reduction with zinc dust or sodium sulphide. A crystalline sulphur dye is obtained by heating in aqueous or alcoholic solution either 1 : 2-dihydroxy-1′ : 4′-dimethyldiphenylamine or its indophenol with sodium sulphide and sulphur. The sodium salt of the dye separates in sparingly soluble, brown, metallic crystals; the free acid is a reddish-violet precipitate; it dyes unmordanted wool in the presence of sodium sulphide to a fast, deep violet shade. G. T. M.

Di-α-naphthyl Selenide and Telluride. ROBERT E. LYONS and G. C. BUSH (*J. Amer. Chem. Soc.*, 1908, **30**, 831—836).—The work described in this paper was undertaken in connexion with a study of the periodic relationship in the oxygen group of elements.

Di-α-naphthyl selenide, $Se(C_{10}H_7)_2$, m. p. 114°, obtained by heating selenium with mercury di-α-naphthyl (compare Krafft and Lyons, Abstr., 1894, i, 448), forms lustrous, pale yellow leaflets and decomposes rapidly on exposure to air and light. It is converted by bromine into the *dibromide*, $Se(C_{10}H_7)_2Br_2$, m. p. 183° (decomp.), which crystallises in white needles. The *dichloride*, $Se(C_{10}H_7)_2Cl_2$, m. p. 130°, forms colourless prisms.

Di-α-naphthyl telluride, $Te(C_{10}H_7)_2$, m. p. 126·5°, crystallises in lustrous, brownish-yellow leaflets. The *dibromide*, m. p. 244° (decomp.), crystallises in lemon-yellow granules, and the *dichloride*, m. p. 265°, in colourless granules.

Diphenyl telluride *dichloride*, $Te(C_6H_5)_2Cl_2$, m. p. 160°, forms long, white prisms. Di-β-naphthyl selenide *dichloride*, m. p. 146°, crystallises in almost colourless leaflets.

A list of aromatic sulphides, selenides, and tellurides, and their halogen additive compounds, is given together with their m. p's. or b. p's., and shows that the change in b. p. or m. p. generally, but not always, varies directly with the atomic weight. With *o*-tolyl sulphide, selenide, and telluride, the reverse is the case, these substances having m. p's. 64°, 62°, and 38° respectively. The m. p's. of the halogen additive compounds are very irregular. E. G.

Preparation of Benzyl Alcohol from Benzaldehyde and Potassium Hydroxide. JAKOB MEISENHEIMER (*Ber.*, 1908, **41**, 1420—1422).—For the purification of benzyl alcohol obtained by the Cannizzaro method, Fischer recommends shaking of the ethereal extract with a solution of sodium hydrogen sulphite before drying and distillation. This leads to an extensive conversion of the alcohol into benzyl ether during the distillation; this is due to the presence of small quantities of sulphuric acid. The defect is easily remedied by washing the ethereal solution with an alkali hydroxide after the treatment with sodium hydrogen sulphite. C. S.

"Unsaponifiable Matter" of Laurel Oil. HERMANN MATTHES and HEINRICH SANDER (*Arch. Pharm.*, 1908, **246**, 165—177).—The chief object of this investigation was to determine the nature of the resinous unsaponifiable matter, which various investigators have recorded as a constituent of the oil. The expressed oil used, after being freed from 2·43% of volatile oil, had the following constants: acid number, 9·4; saponification number, 200·9; Reichert-Meissl number, 3·2; Polenske number, 2·8; Hehner number, 85·8 (corrected for unsaponifiable matter); Hübl number, 82·2—82·4; "real" acetyl number, 5·108; "apparent" acetyl number, 15·33, and n_D^{40} 1·4643.

Eighty grams of unsaponifiable matter were obtained from 8 kilos. of oil, and this was found to consist of a mixture of myricyl alcohol with the following substances: (1) a *phytosterol*, $C_{27}H_{44}O,H_2O$, m. p. 132—133°, which crystallises in colourless needles and furnishes a crystalline *acetyl* derivative, m. p. 125°, which yields an amorphous *dibromide*, m. p. 130°; (2) *laurane*, $C_{20}H_{42}$, m. p. 69°, which crystallises from alcohol in slender needles and is readily soluble in light petroleum, benzene, or boiling alcohol, and (3) an aromatic, unsaturated oily substance. Laurane may be identical with the bryonane found by Etart in the leaves of *Bryonia alba* (*Ber.*, 1892, **25**, 287). The colour reactions given by the phytosterol are tabulated in the original in comparison with those given by phytosterols from other sources.

T. A. H.

Spongosterol, the Cholesterol from Suberites domuncula. Martin Henze (*Zeitsch. physiol. Chem.*, 1908, **55**, 427—432. Compare Abstr., 1904, i, 410).—Spongosterol forms an acetate, m. p. 124·5°, which on treatment in ethereal solution with bromine dissolved in glacial acetic acid yields a *monobromo*-derivative; this, after recrystallisation from glacial acetic acid and alcohol, melts at 157°. On reduction of this substance with zinc dust and glacial acetic acid, spongosteryl acetate is regenerated. Spongosterol appears to be a saturated compound of the formula $C_{27}H_{48}O$. The other derivatives prepared were *bromoacetylspongosterol*, m. p. 171° (by the action of bromoacetyl chloride), *spongosteryl chloride*, m. p. 91° (by the action of phosphorus pentachloride), and *spongostene*, a hydrocarbon obtained from spongosteryl chloride by the action of sodium and amyl chloride.

S. B. S.

Preparation of Aromatic Ethanolamines. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 193634).—The cyanohydrins of the aromatic aldehydes and ketones can be reduced with sodium amalgam (4% Na) to the corresponding ethanol bases. During the reduction, the solution is maintained as far as possible in the neutral condition by the addition of dilute acetic acid. In this way, *anilinomethylcarbinol* was produced from benzaldehyde cyanohydrin, and obtained as a colourless oil which slowly solidified; *hydrochloride*, soluble crystals, m. p. 176—177°, and *picrate*, m. p. 153—154°.

Protocatechualdehyde cyanohydrin, $C_6H_4(OH)_2\cdot CH(OH)\cdot CN$, reddish-brown crystals, m. p. 100—105°, on reduction in the foregoing manner furnishes *dihydroxyphenylaminomethylcarbinol*,

$$C_6H_3(OH)_2\cdot CH(OH)\cdot CH_2\cdot NH_2,$$

white crystals, m. p. 191°.

G. T. M.

Preparation of Halogen Derivatives of Alkyl Carboxylates. EMANUEL MERCK (D.R.-P. 192035).—The halogen derivatives,

$$R\cdot CO\cdot O\cdot[CH_2]_x\cdot X,$$

of the alkyl carboxylates (where X is a halogen and R a hydrocarbon residue) are produced by condensing the monoalkyl carboxylates, $R\cdot CO_2$, with excess of the dihalide ethers, $X\cdot[CH_2]_x\cdot X$.

γ-Bromopropyl benzoate, $Ph\cdot CO\cdot O\cdot CH_2\cdot CH_2\cdot CH_2Br$, colourless oil, b. p. 147—149°/6 mm., is obtained by condensing trimethylene bromide and dry sodium benzoate at 170—180°.

ε-Bromoamyl benzoate, $Ph\cdot CO_2\cdot[CH_2]_4\cdot CH_2Br$, pale yellow oil, b. p. 185—187°/5 mm., *ε-bromoamyl* p-*nitrobenzoate*,

$$NO_2\cdot C_6H_4\cdot CO_2\cdot[CH_2]_4\cdot CH_2Br,$$

greenish-yellow needles, m. p. 45—46°, *ε-bromoamyl salicylate*,

$$OH\cdot C_6H_4\cdot CO_2\cdot[CH_2]_4\cdot CH_2Br,$$

b. p. 193°/3 mm., and 3-*bromoamyl anisate*,

$$OMe\cdot C_6H_4\cdot CO_2\cdot[CH_2]_4\cdot CH_2Br,$$

oil, b. p. 215—217°/3 mm., are prepared from αε-dibromopentane and the sodium salt of the corresponding aromatic acid (benzoic, salicylic, &c.). G. T. M.

Catalysis. IV. Catalysis of Imino-esters. IRA H. DERBY (*Amer. Chem. J.*, 1908, **39**, 437—473).—Stieglitz (this vol., ii, 167, 168) has given an account of the catalysis of imino-esters. The present paper deals with the experimental work on which his conclusions were based.

The imino-esters were prepared by a modification of Pinner's method. Ethyl iminobenzoate has b. p. 101—102°/11 mm., 115°/21·5 mm., and 219°/744·7 mm. (decomp.), n^{20} 1·5278, and is soluble in 100 c.c. of water to the extent of 0·396 gram; the partition coefficient between water and carbon tetrachloride has been determined at 23°. Methyl iminobenzoate has b. p. 91·8°/11 mm. and 106°/22 mm., n^{20} 1·5430, and is slightly more soluble in water than the ethyl ester. Propyl iminobenzoate has b. p. 121°/16 mm., n^{20} 1·5173, and is less soluble in water than either the ethyl or the methyl ester. iso*Propyl iminobenzoate* has b. p. 102°/10 mm. and 114°/20 mm., n^{20} 1·5144, and dissolves in water to the extent of 0·161 gram in 100 c.c. *Methyl* m-*nitroiminobenzoate*, m. p. 50·6°, is a pale yellow solid, which is very slightly soluble in water; the aqueous solution has a conductivity 4×10^{-6} at 25°.

The affinity constants of the esters, the velocity of decomposition of their hydrochlorides, the effect of temperature and of excess of hydrochloric acid on their velocity of decomposition, and the velocity of reaction of the free imino-esters in aqueous solution have been determined and the results are tabulated. E. G.

Resolution of Aminophenylacetic Acid into Optically Active Constituents. EMIL FISCHER and OSKAR WEICHHOLD (*Ber.*, 1908, **41**, 1286—1295).—The Walden rearrangement has been further studied in the case of optically active phenylacetic acid, in which the asymmetric group is between the electronegative phenyl and the carboxyl. Aminophenylacetic acid can be resolved by means of the quinine and cinchonine salts of its formyl derivative; previously, only the *l*-form had been obtained by Ehrlich (this vol., i, 268) by partial fermentation of the racemic compound. The active acid in presence of either nitrous acid or nitrosyl bromide is so rapidly racemised that no pure optically active products could be isolated. The near position of the phenyl group apparently favours racemisation in this case, as with phenylalanine under like conditions there is comparatively little change.

dl-*Formylaminophenylacetic acid*, $CHO\cdot NH\cdot CHPh\cdot CO_2H$, crystallises in stellar aggregates of microscopic needles, which sinter at 176·5°, m. p. 180° (corr. decomp.). The *cinchonine* salt of the *l*-formyl compound crystallises out first in well-formed, colourless, often centimetre-long prisms. l-*Formylaminophenylacetic acid* crystallises in microscopic, thin plates from water, or in bunches of tiny needles from alcohol, m. p. 190° (corr. decomp.), and has $[\alpha]_D^{20}$ $-259·8°$. To purify the *d*-compound, the *quinine* salt is first isolated in silky, glistening, colourless needles; the *d*-acid has $[\alpha]_D^{20}$ $+259·4°$; the formyl compounds are hydrolysed by heating with 10% hydrobromic acid.

l-Aminophenylacetic acid (compare Ehrlich, *loc. cit.*) has m. p. 305—310° (corr.), dissolves in 70 parts of hot water and 207 parts at 25°, and has $[\alpha]_D^{20}$ $-157·8°$. The *hydrobromide* and *hydrochloride* form large, colourless needles, the latter have m. p. 246° (corr. decomp.). The *ethyl* ester is an oil, but forms a *hydrochloride*, m. p. 203° (corr.), $[\alpha]_D^{20}$ $+88·95°$. d-*Aminophenylacetic acid* has similar properties; $[\alpha]_D^{20}$ $+157·9°$.

By the action of nitrous acid, inactive mandelic acid was obtained equally from the racemic or the active acids. Similarly, in the case of the ethyl ester, only very feebly active products resulted; better results, however, are indicated by the use of the amyl ester.

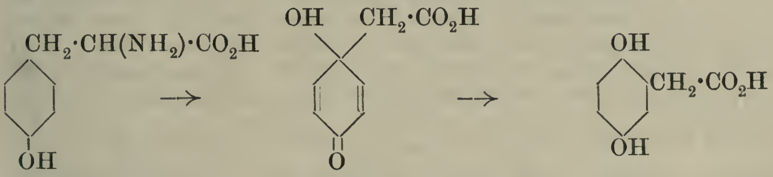
E. F. A.

Synthesis of Polypeptides. XXIV. Derivatives of 2:5-Di-iodo-*l*-tyrosine. Emil Abderhalden and Markus Guggenheim (*Ber.*, 1908, **41**, 1237—1243).—Polypeptides containing iodine substituted tyrosine are of considerable interest on account of their wide distribution in the organic skeleton of *Anthozoa*. Iodogorgonic acid, derived from coral, has been shown by Wheeler and Jamieson (Abstr., 1905, i, 350) to be identical with 2:5-di-iodotyrosine.

2:5-*Di-iodo*-l-*tyrosine*, prepared by the action of iodine on *l*-tyrosine, derived from silk fibrin, by Wheeler and Jamieson's method, has m. p. 213° (corr.), and $[\alpha]_D$ $+2·27°$ in dilute ammonia and $[\alpha]_D^{20}$ $+2·89°$ in 4% hydrochloric acid. *Di-iodotyrosine methyl ester hydrochloride*, formed by the action of dry hydrogen chloride on a suspension of the acid in methyl alcohol, forms colourless needles, decomp. 210·9° (corr.); the corresponding *nitrate* crystallises in long needles. The free *ester* crystallises in glistening plates, decomp. 192° (corr.).

Coupled with chloroacetyl chloride in chloroform solution, it yields *chloroacetyldi-iodotyrosine methyl* ester; this forms tiny, prismatic needles, which sinter at 146°, m. p. 149° (corr.). *Chloroacetyldi-iodotyrosine*] $CH_2Cl\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_2I_2\cdot OH$, obtained on hydrolysis of the ester with sodium hydroxide, crystallises in prismatic needles arranged in stellar aggregates, which become brown at 218°, decomp. 221° (corr.). *Glycyl-*2 : 5-*di-iodotyrosine*, prepared either by the action of aqueous ammonia on chloroacetyldi-iodotyrosine or by that of iodine on glycyl-*l*-tyrosine, has decomp. 232° (corr.), and $[\alpha]_D^{20}$ $+51{\cdot}20°$ to $+52{\cdot}69°$. The *hydrochloride* of the *methyl* ester forms minute needles, decomp. 185° (corr.). *Glycyldi-iodotyrosine methyl ester* sinters at 85·5°, decomp. 130° (corr.). E. F. A.

The Degradation of Carboxylic Acids in the Animal Body. VI. Ernst Friedmann (*Beitr. chem. Physiol. Path.*, 1908, **11**, 304—307).—The conversion of tyrosine into homogentisic acid in alcaptonuric individuals can only be explained by a change of position of the hydroxyl group in relation to the acid group in the benzene ring. Zincke, Auwers, and Bamberger have shown that such a change can take place in the case of the methyl group in certain quinol derivatives. It is suggested that quinol-like substances can be formed as intermediate products between tyrosine and homogentisic acid, and that a wandering of the acetic acid group can take place.

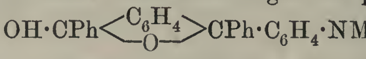


(I.) (II.) (III.)

To test this hypothesis, ethyl *p*-hydroxylaminophenylacetate has been prepared. This substance should, by the Bamberger reactions, be convertible into substances of formulæ II and III. It was obtained by reducing the ethyl *p*-nitrophenylacetate in alcoholic solution with zinc dust and aqueous ammonium chloride. It melts at 64·5°, and gives, after treatment with sulphuric acid, the typical quinol reactions. S. B. S.

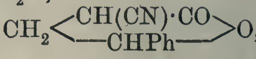
Preparation of Anthroxanic Acid. Kalle & Co. (D.R.-P. 191855).—*o*-Nitromandelic acid, when reduced with sufficient zinc dust and ammonium chloride to furnish the nitroso-derivative, gives rise to a moderately soluble acid, which melts at 130—135°, and at higher temperatures evolves carbon dioxide and furnishes a certain amount of isatin. This product is not identical with nitrosomandelic acid, for, unlike the latter, it is transformed by treatment with aqueous sodium hydroxide into sodium anthroxanate, this reaction being indicated by a change in the colour of the solution from violet to light yellow. On acidifying this liquid, the anthroxanic acid separates in white, sandy crystals. G. T. M.

Preparation of Methylenecitryloxytoluic Acids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 193114. Compare Abstr., 1907, i, 1045).—The products of the action of methylenecitryl chloride on the hydroxytoluic acids have the same valuable therapeutic properties as methylenecitrylsalicylic acid. The condensation is effected in an anhydrous medium, for instance, benzene or chloroform in the presence of a tertiary base, such as quinoline or dimethylaniline, or the alkali salt of the acid may be condensed with the chloride. The following compounds were prepared: *methylenecitryloxy*-p-*toluic acid*, colourless crystals, soluble in alcohol, ethyl acetate, or ether, insoluble in water or petroleum, m. p. 175—178°; *methylenecitryloxy*-m-*toluic acid*, m. p. 179°; *methylenecitryloxy*-o-*toluic acid*, m. p. 170°; *methylenecitryloxy*-o-*toluic acid*, m. p. 170—175°. The last three melt indefinitely with decomposition. G. T. M.

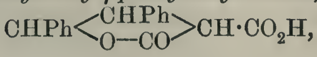
Action of Magnesium Phenyl Bromide on the Second Methyl Ester of *p*-Dimethylamino-*o*-benzoylbenzoic Acid. J. Pérard (*Compt. rend.*, 1908, **146**, 934—936).—Adopting the method employed by Meyer (Abstr., 1904, i, 747) for preparing the methyl ester of the tautomeric form of *o*-benzoylbenzoic acid (Haller and Guyot, Abstr., 1901, i, 146), the author has prepared a second methyl ester of *p*-dimethylamino-*o*-benzoylbenzoic acid. The new *methyl* p-*dimethylamino*-o-*benzoylbenzoate*, m. p. 116°, crystallises in large, silky leaves, readily soluble in benzene, sparingly so in ether; the isomeride prepared by Haller and Guyot (Abstr., 1894, i, 602) has m. p. 118° (those authors there gave 128°). The new methyl *p*-dimethylamino-*o*-benzoylbenzoate reacts with magnesium phenyl bromide to form the compound  $OH\cdot CPh<\begin{matrix}C_6H_4\\O\end{matrix}>CPh\cdot C_6H_4\cdot NMe_2$, m. p. 194° (uncorr.), which is also similarly obtained from the isomeric methyl ester, m. p. 118° (Abstr., 1906, i, 755). M. A. W.

Fixation of Hydrogen Cyanide by Benzoylacrylic Acid. J. Bougault (*Compt. rend.*, 1908, **146**, 936—937).—Benzoylacrylic acid (this vol., i, 179, 269) combines with hydrogen cyanide to form α-cyano-β-benzoylpropionic acid, $COPh\cdot CH_2\cdot CH(CN)\cdot CO_2H$, identical with cyanophenacylacetic acid (Klobb, Abstr., 1894, i, 592; 1896, i, 126); the m. p's. of the hydrated and anhydrous acids are 70° and 103° respectively (Klobb gives 69° and 99—100°), and on reduction with sodium amalgam the acid yields the corresponding hydroxy-acid, *α-cyano-γ-hydroxy-γ-phenylbutyric acid*,

$$OH\cdot CHPh\cdot CH_2\cdot CH(CN)\cdot CO_2H,$$

which is readily converted into the *lactone*,  $CH_2<\begin{matrix}CH(CN)\cdot CO\\CHPh\end{matrix}>O$, m. p. 132°.

When α-cyano-β-benzoylpropionic acid is hydrolysed, it is converted into the corresponding dibasic acid, α-carboxy-β-benzoylpropionic acid (β-benzoyl*iso*succinic acid), $COPh\cdot CH_2\cdot CH(CO_2H)_2$ (Kues and Paal, Abstr., 1886, 354); this acid has m. p. 174° (Kues and Paal give 178—179°), and on reduction with sodium amalgam furnishes the *lactone* of *α-carboxy-γ-hydroxy-γ-phenylbutyric acid*,



$$CHPh<\begin{matrix}CHPh\\O-CO\end{matrix}>CH\cdot CO_2H,$$

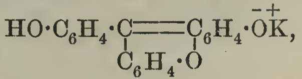
m. p. 106°. M. A. W.

Santonin. Joseph Klein (*Ber.*, 1908, **41**, 1094—1095).—Polemical. A reply to Wedekind (this vol., i, 183. Compare Abstr., 1907, i, 421).
W. R.

Theory of Indicators and the Reactions of Phthaleins and their Salts. Salomon F. Acree (*Amer. Chem J.*, 1908, **39**, 528—544).—A continuation of the controversy with Stieglitz.

The theory of indicators proposed by Stieglitz (Abstr., 1904, ii, 17) is criticised, and it is pointed out that the quinone hypothesis alone is inadequate. In the case of such compounds as the salts of phenolphthalein and aurin, the chief source of colour is not the quinone complex, but the phenol salt of a quinone compound, or a quinonephenoxide group, which may exist in two forms,

$$(\overset{+}{H}\overset{-}{O}\cdot C_6H_4)(\overset{+}{K}\overset{-}{O}\cdot C_6H_4)C\colon C_6H_4\colon O$$ and



$$\begin{array}{l} HO\cdot C_6H_4\cdot C{=\!=\!=}C_6H_4\cdot \overset{-}{O}\overset{+}{K}, \\ \qquad\qquad\quad\; | \qquad\quad | \\ \qquad\qquad\quad C_6H_4\cdot O \end{array}$$

in equilibrium, and the change from one to the other, or a corresponding movement of ions, is probably connected with the colour changes. Again, in the case of rosaniline and similar compounds, the principal cause of the colour is not the quinone group, but the double compound (or "quinaminone") formed by the inter- or intra-molecular union of the quinone complex with the free aniline (or phenylammonium hydroxide) groups of the dye. Evidence is brought forward in support of these views. In all cases, a small amount of colour is, of course, due to the quinone group, since all quinones are somewhat coloured. E. G.

Preparation of Aldehydes from Aromatic Compounds containing the Group C_3H_5 by Oxidation with Ozone. Edward Charles Spurge (D.R.-P. 192565).—A stream of ozonised air is passed through a mixture of 75 parts of *iso*eugenol, 50 parts of sodium hydrogen sulphite solution, and fifty parts of water. Additional sulphite is added from time to time. The soluble vanillin bisulphite is produced. *iso*Safrole and anethole are similarly oxidised to piperonaldehyde and anisaldehyde.
G. T. M.

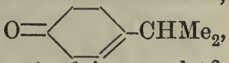
Preparation of the Cyclic Carbonate of Protocatechuic Acid. Hermann Pauly (D.R.-P. 190788).—Piperonaldehyde is converted into protocatechualdehyde by successive chlorination and hydrolysis with water. In the first step of the process, ω-dichloropiperonaldehyde is produced, which then reacts with 2 mols. of water. By treating this substance with only 1 mol. of water, the two chlorine atoms of the side-chain are replaced by one of oxygen, and the cyclic carbonate of protocatechualdehyde (Abstr., 1907, i, 709) is produced. This product forms colourless triclinic crystals, m. p. 122°, and b. p. 160°/13 mm. and 289°/760 mm. The removal of chlorine is effected by heating dichloropiperonaldehyde with anhydrous oxalic acid at 120—130°, concentrated formic acid at 80—90°, or succinic acid at 160—170°.
G. T. M.

Condensation Products of Cyclic Ketones with Aromatic Aldehydes. OTTO WALLACH, H. MALLISON, and K. MARTIUS (*Chem. Zentr.*, 1908, i, 637—639; from *Nachr. K. Ges. Wiss. Göttingen*, 1907, 399—405).—With the object of verifying some observations on the condensation of terpene ketones with benzaldehyde, the authors have investigated the behaviour of cyclic ketones on condensation with aromatic aldehydes. It is found that condensation does not take place with pure ortho substituted ketones; indeed, this is a method of purification from other ketones. The spacial configuration of the molecules appears to influence the possibility of condensation. Considerable difference is observed in the behaviour of the three nitrobenzaldehydes: *m*-nitrobenzaldehyde condensing very readily, the *p*-compound with some difficulty, whilst the *o*-compound does not condense at all, although *o*-chlorobenzaldehyde gives the reaction. The conditions under which condensation is carried out play an important part in determining the nature of the resulting product; thus benzaldehyde in very dilute aqueous solution in presence of excess of ketone gives in some cases the first product of condensation, the aldol. From benzaldehyde and *cyclo*hexanone, the *monoaldol*, m. p. 101—102°, and the *dialdol*, m. p. 161—162°, have been prepared; also from inactive 1:3-methyl*cyclo*hexanone, the *monoaldol*, m. p. 106—107°, and from 1:4-methyl*cyclo*hexanone, the *monoaldol*, m. p. 127°. Active and inactive 1:3-methyl*cyclo*hexanone behave differently, the latter only giving a well-defined aldol. In some cases, it is found that condensation takes place more readily in presence of excess of formic acid or acetic anhydride than with alkaline alcoholic solutions; dilute potassium cyanide solution may also be used instead of sodium hydroxide. Generally, the condensation products are yellow to orange in colour, and dissolve in concentrated sulphuric acid, exhibiting colour changes apparently dependent on the nature of the aldehyde employed. A table of the melting points of 65 condensation products is appended. J. V. E.

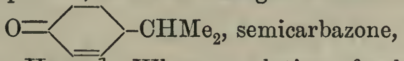
Mesitylenetrialdehyde (1:3:5-Trimethylalbenzene). JEAN BIELECKI (*Bull. Acad. Sci. Cracow*, 1908, 29—32).—The oxidation of mesitylene with chromic anhydride in presence of acetic anhydride and sulphuric acid (compare Thiele and Winter, Abstr., 1900, i, 500) yields *mesitylenetrialdehyde hexa-acetate*, $C_6H_3[CH(OAc)_2]_3$, slender needles from methyl alcohol, m. p. 125—126° (corr.). When boiled with 4% hydrochloric acid, it yields *mesitylenetrialdehyde*, m. p. 94°. No analysis of this compound was made.

Tetra-ω-chloro-m-*xylene*, $C_6H_4(CHCl_2)_2$, was prepared by the action of chlorine on boiling *m*-xylene in presence of aluminium chloride, extracting with alcohol, and boiling with animal charcoal. It forms slender, silky needles, m. p. 223—223·5° (corr). A. J. W.

Terpenes and Ethereal Oils. XC. OTTO WALLACH (*Annalen*, 1908, 359, 2652—86).—*Transformation of Sabina ketone, and a Synthesis of a-Phellandrene.*—New methods of preparing sabina ketone are given: (1) from sabinene by oxidation, and (2) from sodium sabinenate by oxidation. Sabina ketone differs from nopinone by being more soluble in water and solidifying more readily, forming prismatic crystals, m. p. 17°. Once solidified, it is a solid at the ordinary temperature, but readily remains liquid, having b. p. 218—219°, D^{20} 0·9555, $[\alpha]_D$ $-24°41'$, n_D^{20} 1·4704. The *semicarbazone* is very readily soluble in alcohol, from which it separates in a gelatinous form, m. p. 135—137° (compare Semmler, Abstr., 1902, i, 550); from dilute methyl alcohol, it separates in hard crystals, m. p. 141—142°. Oxalic acid decomposes this semicarbazone, giving substantially unaltered sabina ketone; sulphuric acid yields *iso*propyl*cyclo*hexenone, only a trace of the hydrocarbon, C_9H_{14}, mentioned by Semmler (*loc. cit.*) being observed. When heated with dilute sulphuric acid, sabina ketone gives a yellow oily product, from which *iso*propyl*cyclo*hexenone is separated by distillation with steam. Sabina ketone isomerises under the influence of acids, chiefly forming 1-iso*propyl*-Δ^1-cyclo*hexen*-4-*one*,

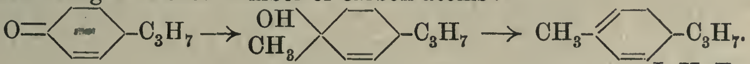


semicarbazone, m. p. 170°, and this changes further to 1-*iso*propyl-Δ^2-*cyclo*hexen-4-one,



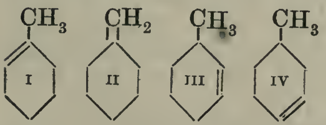
semicarbazone, m. p. 180°.

[With Richard Heyer]—When a solution of sabina ketone in a mixture of alcohol and ether is saturated with dry hydrogen chloride, the *compound*, $C_9H_{15}OCl$, is obtained, which separates from ether in clear, prismatic crystals, m. p. 77—78°. In glacial acetic acid solution, dry hydrogen chloride forms the compound, $C_{18}H_{29}OCl_3$, which crystallises from ethyl acetate, m. p. 124°. Hydrogen chloride may be removed from the monochloride, m. p. 77—78°, in both possible ways, giving *iso*propyl-Δ^1-*cyclo*hexenone and 4-*iso*propylidene*cyclo*hexenone (Trans., 1907, 91, 1746), which were both identified by their semicarbazones. *iso*Propyl-Δ^1-*cyclo*hexenone, when warmed with mineral acids, undergoes a change to iso*propyl*-Δ^2-cyclo*hexenone*, b. p. 217—221°, $[\alpha]_D+2·15°$, D^{19} 0·947, n_D^{19} 1·4807. Treated with magnesium methyl iodide, *iso*propyl-Δ^2-hexenone yields α-phellandrene together with small quantities of an alcohol, b. p. 208—211°, D^{19} 0·9230, n_D^{19} 1·4760; this is the first synthesis of phellandrene from a substance containing a smaller number of carbon atoms:



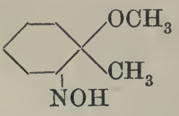
J. V. E.

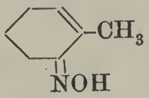
Terpenes and Ethereal Oils. XCI. Otto Wallach (*Annalen*, 1908, 359, 287—316. Compare Abstr., 1907, i, 1061).—*Isomeric Hexacyclic Hydrocarbons*, C_7H_{12}.—The author reviews the characteristic reactions of I and II of the following four isomeric substances, and gives further that I, by moderate oxidation with potassium permanganate, yields a *glycol*, m. p. 67°, which when warmed with acid is converted into 1-methyl*cyclo*hexan-2-one.

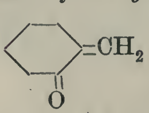


The nitrosochloride, m. p. 127°, from II readily loses hydrogen chloride, forming an *aldoxime*, crystallising from light petroleum, m. p. 97—99°, and this yields a *benzoyl* derivative, m. p. 101—102°. When warmed with acids, the oxime gives tetrahydrobenzaldehyde. Hydrogen chloride, passed into a glacial acetic acid solution of methylene*cyclo*hexane, produces a *chloride*, b. p. 151—152°. When heated with a mixture of glacial acetic acid and sulphuric acid, the *acetate* is produced. Methyl-Δ^1-*cyclo*hexene has been prepared from 1-methyl-1-*cyclo*hexanol by the action of anhydrous zinc chloride; it has b. p. 111—112°, D^{20} 0·811, n_D^{20} 1·4496. Further, to characterise this substance, it was oxidised with permanganate, whereby a volatile and a non-volatile product were obtained. The former readily gives a sparingly soluble semicarbazone, crystallises from methyl alcohol, m. p. 202—203°, and is probably identical with the compound, $C_7H_{10}O$, prepared by the oxidation of Δ^1-*cyclo*hexeneacetic acid (Abstr., 1906, i, 176). The non-volatile product contains 1-methyl*cyclo*hexan-1 : 2-diol, which separates from ether in small crystals, m. p. 67°, also δ-acetylvaleric acid, and probably adipic acid.

This new glycol, m. p. 67°, is decomposed by warming with concentrated oxalic acid solution or dilute sulphuric acid, giving 1-methyl-2-*cyclo*hexanone, which is identified by converting to the semicarbazone. When the glycol (m. p. 67°) from methyl-Δ^1-*cyclo*hexene is ground together with the glycol (m. p. 76—77°) from methylene*cyclo*hexane, the mixture becomes semi-fluid at the ordinary temperature. The nitrosochloride from 1-methyl-Δ^1-*cyclo*hexene was prepared and treated with sodium methoxide, whereby a solid and a liquid product were obtained. The solid portion is the *methoxyl-oxime* (annexed formula), which crystallises from light petroleum in small plates, m. p. 64—65°; it gives a *benzoyl* derivative, crystallising from dilute methyl alcohol in leaflets, m. p. 97—98°. The liquid portion yields on extraction with ether a liquid which forms a solid sodium derivative, and this on benzoylation gives two products, one sparingly, the other easily, soluble in ether. The readily soluble substance is the *benzoyl-methoxyl-oxime*, m. p. 97—98°; the less soluble product is the benzoyl derivative of the normal unsaturated oxime (annexed formula). This substance is slightly soluble in methyl alcohol, crystallising in needles, m. p. 142—143°. 1 : 4-Methyl*cyclo*hexanol, when heated with anhydrous zinc chloride, yields a substance, C_7H_{12}, b. p. 106—107°, D^{22} 0·7935, n_D^{22} 1·4384 which proves to be a mixture of methyl-Δ^1-*cyclo*hexene and methyl-Δ^3-*cyclo*hexene. 1-Methyl-2-*cyclo*hexanol treated in a similar manner gives methyl-Δ^1-*cyclo*hexene. When Δ^1-*cyclo*hexeneacetic acid, m. p. 38°, is heated with potassium hydroxide, Δ^a-*cyclo*hexeneacetic acid (Abstr., 1907, i, 616) is not obtained, but δ-acetylvaleric acid and a substance, $C_7H_{10}O$, shown to be neither tetrahydrobenzaldehyde nor methyl-Δ^1-*cyclo*hexenone (Abstr., 1906, i, 176), but probably the ketone (annexed formula). This substance, b. p. 172—174°, D^{17} 0·9445, n_D^{17} 1·4719, gives a *semicarbazone*, m. p. 202—204°, an *oxime*, m. p. 90—91°, and a *benzoyloxime*, m. p. 116—117°.







The behaviour of β-*cyclo*hexylethylamine towards nitrous acid has been studied. *cyclo*Hexylacetonitrile, b. p. 215°, D^{18} 0·913, n_D^{18} 1·4575, on reduction yields β-*cyclo*hexylethylamine, b. p. 188—189°, D^{19} 0·8700, n_D^{18} 1·4647, which gives a hydrocarbon, b. p.

132—137°, and the primary and secondary *alcohols*, $C_6H_{11}\cdot CH_2\cdot CH_2\cdot OH$ and $C_6H_{11}\cdot CHMe\cdot OH$, when treated with sodium nitrite in acid solution. These alcohols were identified by oxidising and converting to the *semicarbazones*, m. p. 132—134° and 172—173° respectively.
J. V. E.

Action of Phthalic Anhydride on Resacetophenone. Henry A. Torrey and C. M. Brewster (*J. Amer. Chem. Soc.*, 1908, **30**, 862—863).—Torrey and Kipper (this vol., i, 460) have stated that when diacetylquinol or diacetylresorcinol is treated with *m*-nitrobenzoyl chloride, the acetyl groups are replaced by *m*-nitrobenzoyl groups. An even more remarkable reaction has been observed, in which the acetyl group in resacetophenone, which, in this case, is directly attached to the ring, is replaced by a group of higher molecular weight. It has been found that when resacetophenone (2 mols.) is heated with phthalic anhydride (1 mol.) in presence of a dehydrating agent, acetic acid is produced and a large yield of fluorescein is obtained. E. G.

An old Derivative of Benzanthrone. Carl Liebermann and K. Roka (*Ber.*, 1908, **41**, 1423—1427).—A comparison of the physical properties and general behaviour of the substance, $C_{19}H_{14}O$, obtained by Liebermann by the action of concentrated sulphuric acid on amyloxanthranol (Abstr., 1882, 855), with those of benzanthrone (compare Bally, Abstr., 1905, i, 237) indicates that the substance must be a derivative of the latter. The analytical data correspond also with the formula $C_{18}H_{14}O$ or $C_{18}H_{12}O$, according to which the substance may be methyldihydrobenzanthrone or methylbenzanthrone. By oxidation with chromic and acetic and dilute sulphuric acids, it yields, like benzanthrone, anthroquinone-α-carboxylic acid, whilst reduction by hydriodic acid and phosphorus results in the formation probably of the methyl homologue of the *hydrocarbon*, $C_{17}H_{16}$ or $C_{17}H_{14}$, m. p. 80°, obtained by the reduction of benzanthrone in a similar manner. Both hydrocarbons yield colourless solutions in concentrated sulphuric acid which become red on warming. C. S.

Some Derivatives of Tetrachloro-*o*-benzoquinone. C. Loring Jackson and P. W. Carleton (*Amer. Chem. J.*, 1908, **39**, 493—505).—In an earlier paper (Jackson and MacLaurin, Abstr., 1907, i, 856), an account was given of the reactions of tetrachloro-*o*-benzoquinone with alcohols, toluene, glacial acetic acid, and other substances.

In continuation of this work, it has been found that when equal weights of tetrachloro-*o*-benzoquinone and tetrachlorocatechol are dissolved in the smallest possible quantities of hot chloroform, the solutions mixed, and the mixture rapidly cooled, octachloro-*o*-quinhydrone is produced, but that if the mixture is kept warm for some time, heptachloro-*o*-quinocatechol hemi-ether is formed.

Octachloro-o-benzoquinhydrone, $C_6Cl_4O_2\cdot C_6H_2Cl_4O,\frac{1}{2}H_2O$, m. p. about 160°, forms lustrous, black needles, which readily effloresce, becoming dull and dark purple. The substance turns yellow at 70°, with formation of heptachloro-*o*-quinocatechol hemi-ether. When treated with nitrobenzene, it yields tetrachlorocatechol, tetrachloro-*o*-benzoquinone, the red ether, $C_6Cl_4O_2 \cdot C_6Cl_2O_2$, and heptachloro-*o*-quinocatechol hemi-ether.

*Heptachloro-*o*-quinocatechol hemi-ether*, $C_6Cl_4(OH)O \cdot C_6Cl_3O_2$, m. p. about 214° (decomp.), crystallises in yellow scales.

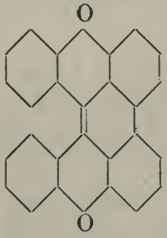
Improved methods are described for the preparation of hexachloro-*o*-quinomethylhemiacetalcatechol ether and hexachloro-*o*-quinodimethylhemiacetalcatechol ether (Jackson and MacLaurin, *loc. cit.*). The acetyl compound described by Jackson and MacLaurin (*loc. cit.*) as melting at 215° has the formula $C_6Cl_4O_2 \cdot C_6Cl_2O(OMe) \cdot OAc$, and m. p. 220°.

When tetrachloro-*o*-benzoquinone is treated with acetophenone, a *compound*, m. p. 281°, is produced. On oxidising tetrachloro-*o*-benzoquinone or tetrachlorocatechol with fuming nitric acid containing a little hydrochloric acid, a yellow substance, m. p. 146—147°, is formed, which is probably identical with the compound obtained by Jackson and MacLaurin (*Amer. Chem. J.*, 1907, **37**, 19) by the prolonged action of chlorine on tetrachlorocatechol. E. G.

Preparation of Dimethyl Ether of *p*-Nitrochrysazin. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 193104. Compare Abstr., 1906, i, 677).—Hitherto the nitration of chrysazin and its ethers have led to the formation of di- and tetra-nitrochrysazins, but the following process furnishes the *dimethyl* ether of p-*nitrochrysazin*. The dimethyl ether of chrysazin was dissolved in cold concentrated sulphuric acid, and treated gradually with nitric acid (27% HNO_3). After twenty-four hours, the mixture was poured on to ice. The product, after crystallisation from chlorobenzene, separated in green needles, m. p. 232—233°.

p-*Nitrochrysazin*, obtained by hydrolysing the dimethyl ether with hot 10% sulphuric acid, separates from chlorobenzene in orange-yellow crystals, m. p. 232—234°. G. T. M.

Preparation of Anthracene Derivatives from α-Dianthraquinonyl. ROLAND SCHOLL (D.R.-P. 190799).—α-Dianthraquinonyl and its derivatives, when treated with acid reducing agents, lose two oxygen atoms and become converted into complex diketo-derivatives, the simplest of which is regarded as having the annexed formula.



This compound, produced by reducing dianthraquinonyl with alcoholic stannous chloride or concentrated sulphuric acid and copper powder (or some other metal, such as nickel, iron, or zinc), is a sparingly soluble, brownish-yellow powder obtained crystalline from xylene or nitrobenzene. G. T. M.

New Borneol. OSSIAN ASCHAN (*Ber.*, 1908, **41**, 1092—1094).—Camphene hydrochloride, when stirred with milk of lime at 50—60° and finally at 80° during twelve to eighteen hours, then subjected to distillation with steam, extraction with ether, and fractionation in small portions after removal of the ether, gives a new borneol in good yield, *camphene hydrate*, $C_{10}H_{18}O$, which, on sublimation, crystallises in strongly refractive tetrahedra, m. p. 150—151°. It has an odour resembling menthol, loses water very easily with dilute mineral acids, or on boiling with glacial acetic acid for a short time, or on distillation of large quantities at 180°, camphene being regenerated. Oxidation leads to the production of small quantities of camphor. The conclusion is drawn provisionally that it is a tertiary alcohol, formed by the replacement of tertiary chlorine by hydroxyl. W. R.

Preparation of Alkyloxyacetyl Derivatives of the Hydroaromatic Alcohols. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 191547).—The therapeutic application of the hydroaromatic alcohols, such as santalol, menthol, and borneol, is attended by the disadvantage that these substances have an intense odour and unpleasant secondary reactions. The alkyloxyacetyl derivatives of these alcohols are tasteless and odourless, and do not exhibit the secondary reactions.

Bornyl ethoxyacetate, $OEt\cdot CH_2\cdot CO\cdot O\cdot C_{10}H_7$, colourless liquid, b. p. 175—178°/20 mm., was prepared by condensing borneol and ethoxyacetyl chloride in benzene solution in the presence of pyridine. *Santalyl ethoxyacetate* is a colourless liquid, b. p. 185—190°/20 mm.

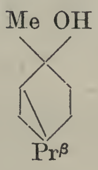
Menthyl methoxyacetate, liquid, b. p. 140°/10 mm., was obtained from menthol, menthoxyacetic acid, and carbonyl chloride in benzene solution. G. T. M.

Preparation of *iso*Bornyl Oxalate. J. Basler & Co. (D.R.-P. 193301).—It has been found that camphene (100 parts) and anhydrous oxalic acid (100 parts) in 300 parts of acetone containing 15 parts of sulphuric acid, when left at 15—25° for three days, furnish a mixture of the acid and normal *iso*bornyl esters of oxalic acid. The unchanged oxalic acid is removed with hot water, and the *iso*bornyl hydrogen oxalate extracted with aqueous sodium carbonate; the latter has not been obtained crystalline. iso*Bornyl oxalate* crystallises from alcohol in colourless, odourless needles, m. p. 113—114°. The unaltered camphene was separated by distillation in steam; when the combination is carried out at 110—115°, this distillate contained both camphene and *iso*bornyl formate. Both the esters are readily hydrolysed, yielding *iso*borneol and oxalic acid. G. T. M.

Terpenes and Ethereal Oils. XCIII. Resolution of Linkings by Addition of Water to Terpene Compounds. Otto Wallach (*Annalen*, 1908, **360**, 82—104).—Although the addition of water to terpene molecules is well known to occur in specific cases, the course of such addition and the relative ease with which it takes place with terpene compounds of different structures have not previously been studied systematically. The investigation of these points has been undertaken, and the first results are now given.

In order that the results might be comparable, the hydration experiments have been carried out in each case, so far as possible, under the same conditions, the terpene compound being shaken with a large excess of 3% to 5% sulphuric acid at the ordinary temperature. The unavoidable differences in the experimental conditions lie in the varying solubilities of the compounds in dilute acid; solubility is, however, not of itself a decisive factor, since substances such as pinene and sabinene, which are both sparingly soluble, behave very differently, whilst nopinol, in spite of its solubility, is regained unchanged from the dilute acid.

In many cases, the hydration is preceded by an intramolecular transformation. Thus sabinene hydrate (I) changes first into active terpinene-4-ol (II), terpineneterpin (III) being formed only as the product of a further reaction. In the same manner, *cis*-terpin (VI) is formed from pinene hydrate (IV), not directly, but by way of active α-terpinol (V). As the terpinene-4-ol and α-terpineol are optically active substances, they cannot have been formed from the glycols (III) and (VI):



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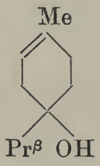

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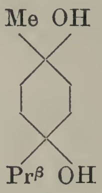

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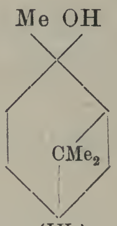

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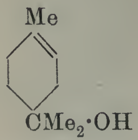

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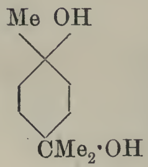

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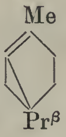

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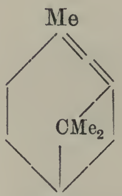

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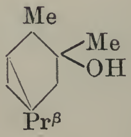

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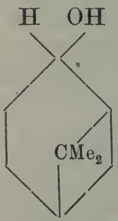
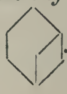
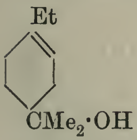


(X.)

It is considered that in such cases, the first stage is loss of water, sabinene hydrate and pinene hydrate forming the unsaturated hydrocarbons (VII) and (VIII), which then add on water, forming terpinene-4-ol and α-terpineol respectively. The ease with which the three-atom ring of (VII), or the four-atom ring of (VIII), is resolved, is ascribed to the influence of the quaternary carbon atom. In agreement with this, it is found that homothujyl alcohol (IX) is extremely stable towards acids; in this, the hydroxyl is differently placed towards the three-atom ring to that of sabinene hydrate, and loss of water cannot lead to the formation of a quaternary carbon atom. On the other hand, whilst methylnopinol (pinene hydrate) is easily attacked by dilute acids, nopinol (X) under the same conditions is stable. This is ascribed to the greater stability of the secondary alcohol grouping. These results agree with Perkin's view (Trans., 1907, 91, 817) that the stability of the *cyclo*propane and *cyclo*butane rings depends much more on the nature and position of the attached groups than on the number of carbon atoms in the ring.

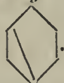
I *Comparative Experiments on the Resolution of Four-Atom Rings by Addition of Water to Substances of the Type* .—Crystalline α- and liquid β-nopinols remain unchanged on prolonged shaking with dilute sulphuric acid. Only in one experiment were indications of the formation of traces of a hydration product observed.

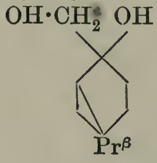
Methylnopinol (pinene hydrate), when shaken with dilute acid for two to three hours, is converted into terpin hydrate, but, if shaken only for one hour, yields *l*-α-terpineol, m. p. 37—38°, b. p. 218—219°, $[\alpha]_D - 106°$. This high rotatory power shows that previous specimens of active α-terpineol have contained more or less of the inactive substance. As methylnopinol is formed from nopinone by Grignard's reaction (Wallach and Blumann, Abstr., 1907, i, 936), its conversion into *l*-α-terpineol completes the first synthesis of an optically active α-terpineol from a substance containing a smaller number of carbon atoms. The synthetical *l*-α-terpineol forms a *nitrosochloride*, crystallising in needles, m. p. 107—108°, and a *nitrolpiperidide*, needles or prisms, m. p. 150°. When oxidised with permanganate, it yields a solid *glycerol*, which on further oxidation by means of chromic acid is converted into a *keto-lactone*, m. p. 46—47°; this forms a *semicarbazone*, m. p. 199°.



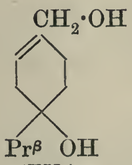
Ethylnopinol (Abstr., 1907, i, 1059), when shaken with dilute acid, is first converted into a *homologue* of α-terpineol, b. p. 226—227°, which has the annexed constitution. Its behaviour is similar to that of α-terpineol, but it unites with water more slowly to form the corresponding terpin hydrate. *n*-Propylnopinol reacts with 3% sulphuric acid in the same manner as ethylnopinol.

Nopic acid does not yield a saturated dihydroxy-acid when treated with cold dilute acid. Nopinone remains unchanged in the cold, but when heated with concentrated sulphuric acid is converted into *iso*propylhexenone, whereas pinocamphone is stable towards boiling acids.

II. *Comparative Experiments on the Resolution of Three-Atom Rings by Addition of Water to Compounds of the Type* .—Thujyl alcohol and *homothujyl alcohol*, $C_{11}H_{20}O_2$, which is prepared from thujone and magnesium methyl iodide, and is obtained in a solid, m. p. 84°, and a liquid modification, remain unchanged when shaken with cold dilute sulphuric acid. Methylsabinaketol (sabinene hydrate), on the other hand, is converted successively into *d*-terpinene-4-ol and terpineneterpin. The higher homologues of sabinene hydrate react in the same manner, but more slowly and less completely. Sabinene glycol (XI) yields an unsaturated glycol, m. p. 105°, which has probably the constitution (XII):



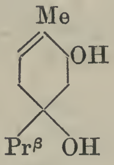
(XI.)



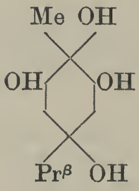
(XII.)

Sabinaglycerol is converted into an unsaturated *glycerol*, $C_{10}H_{18}O_3$, b. p. 200°/10 mm. Thujone remains unchanged in the cold, and is converted into *iso*thujone by hot concentrated acid. Sabina ketone is much more stable than methylsabinaketol towards cold acid, but is converted into *iso*propylhexenone by hot alcoholic sulphuric acid.

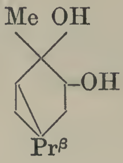
Thujene and sabinene yield terpinene-4-ol and terpineneterpin, the reaction taking place much the more rapidly in the case of sabinene. Sabinol is converted by 5% sulphuric acid in two days into a *glycol* (XIII), which on oxidation with permanganate yields a substance named by the author *erythrit* (XIV); this separates in crystals, m. p. 186°, and has a sweet flavour. The hypothetical intermediate products (XV) and (XVI) are assumed to be formed between sabinol and the glycol:



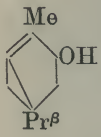
(XIII.)



(XIV.)

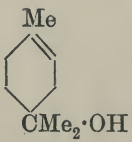


(XV.)

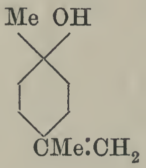


(XVI.)

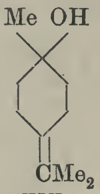
III. *Comparative Experiments on the Resolution of an Ethylene Linking by Addition of Water.*—Of the five isomeric menthenols, β- and γ-terpineols (XVIII) and (XIX) react more readily with dilute sulphuric acid than does α-terpineol (XVII), whilst terpinene-1-ol (XX) and terpinene-4-ol (XXI) react so much more slowly than the terpineols that treatment with dilute acid may be used as a means of separation of these (Abstr., 1907, i, 943). Whilst α- and *s*-terpineols yield ordinary terpin hydrate, and the terpinenol forms terpineneterpin, m. p. 137°, the hydration product of γ-terpineol is a mixture of the two isomerides:



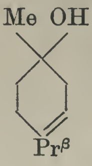
(XVII.)



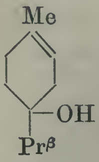
(XVIII.)



(XIX.)



(XX.)

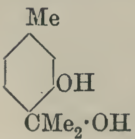


(XXI.)

The resolution of an ethylene linking in a side-chain by addition of water is further illustrated by dihydrocarveol,

$$OH\cdot C_6H_9Me\cdot CMe{:}CH_2,$$

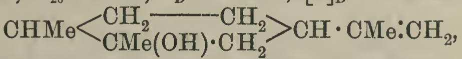
which forms a glycol, $OH\cdot C_6H_9Me\cdot CMe_2\cdot OH$, and by *iso*pulegol, $C_{10}H_{18}O$, which yields a *glycol*, m. p. 75°, having the annexed constitution.

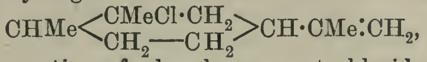


The semicyclic ethylene linking of sabinene is readily resolved by water; the resulting hydrate is unstable, losing water and forming the first intermediate product of sabinene hydrate (VII), and therefore yields finally terpinene-4-ol.

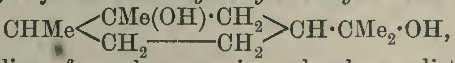
Whilst pinene is slowly acted on by 5% sulphuric acid, limonene and methylene*cyclo*hexane remain unchanged. It is the more remarkable that the hydrocarbon, obtained from water-fennel oil and consisting chiefly of β-phellandrene, yields *cis*-terpin together with small amounts of *trans*-terpin. G. Y.

Action of Magnesium Methyl Halides on Carvone and Dihydrocarvone. HANS RUPE and F. EMMERICH (*Ber.*, 1908, **41**, 1393—1403. Compare Rupe and Liechtenhan, Abstr., 1906, i, 374; Klages and Sommer, *ibid.*, 566; Klages, Abstr., 1907, i, 597).—The authors have obtained a methylmenthatriene with $[\alpha]^{20}_{D}$ +103·49° by the action of acetic anhydride on 2-methylcarveol, a good yield of which is obtained when the additive compound of carvone and magnesium methyl iodide is gradually decomposed with dilute (10—20%) sulphuric acid. When kept for some months, the tertiary alcohol yields the unsaturated hydrocarbon. When distilled several times under reduced pressure, the rotatory power of the hydrocarbon is considerably diminished. When reduced with sodium and amyl alcohol, the hydrocarbon yields a *dihydro*-derivative, *methylmenthadiene*, $C_{11}H_{18}$, b. p. 72°/9 mm., D_{20} 0·8576, n^{20}_{D} 1·46502, $[\alpha]^{20}_{D}$ −55·44°.

2-*Methyldihydrocarveol*,  $\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2}\text{———}\mathrm{CH_2}\\ \mathrm{CMe(OH)\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CMe{:}CH_2}$, obtained by the action of magnesium methyl iodide on dihydrocarvone, is a colourless liquid, b. p. 102—103°/13·5 mm., D_{20} 0·9230, n^{20}_{D} 1·4779. When heated with phthalic acid, it loses water and yields 2-*methylhomolimonene* (2-*methyldihydrocarvene*), $C_{11}H_{18}$, b. p. 77—78°/13·5 mm. and $[\alpha]^{20}_{D}$ −7·99°.

The same product is formed by the action of phosphoric oxide or zinc chloride on the alcohol, but the best yield is obtained by the elimination of hydrogen chloride from the 2-*chloro*-2-*methyl*-$\Delta^{8:9}$-*tetrahydrocymene*,  $\mathrm{CHMe}{<}\begin{matrix}\mathrm{CMeCl\cdot CH_2}\\ \mathrm{CH_2}\text{——}\mathrm{CH_2}\end{matrix}{>}\mathrm{CH\cdot CMe{:}CH_2}$, which can be prepared by the action of phosphorus pentachloride on the alcohol. It is a colourless liquid of pungent odour, and has b. p. 105—108°/10 mm. When heated with quinoline at 200—210°, it yields 2-methylhomolimonene, b. p. 72—74°/10 mm., D_{20} 0·8598, n^{20}_{D} 1·48598, $[\alpha]^{2}_{D}$ −25·33°, and this yields white, crystalline compounds with hydroferro- and hydroferri-cyanic acids, an oily hydrobromide, $C_{11}H_{19}Br$, and does not yield crystalline compounds with nitrosyl chloride, nitrous acid, &c. It is not reduced when treated with sodium and amyl alcohol.

When methyldihydrocarveol is boiled with alcohol and 10% sulphuric acid, it yields 2 : 8-*dihydroxy*-2-*methylmenthane*,



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CMe(OH)\cdot CH_2}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}{>}\mathrm{CH\cdot CMe_2\cdot OH},$$

which crystallises from benzene in colourless, glistening needles, m. p. 135—136°.

The author accepts Klages' formula for methylmenthatriene. J. J. S.

Components of Ethereal Oils. Santalols, $C_{15}H_{24}O$, and their Derivatives. FRIEDRICH W. SEMMLER (*Ber.*, 1908, **41**, 1488—1493. Compare Abstr., 1907, i, 431, 433).—As *tricyclo*santalol, which has one ethylene linking in the side-chain, is obtained mixed with *dicyclo*santalol, containing two ethylene linkings and probably other substances, the preparation of pure *tricyclo*santalaldehyde by oxidation of the *tricyclo*santalol has been attended with many difficulties. The pure aldehyde has now been obtained; its properties and those of its derivatives as now described should be compared with the description given previously (*loc. cit.*).

On oxidation with ozone, crude santalol yields an *oxide*, m. p. 157°, b. p. 114—116°, D^{15} 1·016, n_D 1·50513, nor*tricyclo*santalan, and *tricyclo*santalaldehyde, $C_{11}H_{16}O$, which, after purification by conversion into the sodium hydrogen sulphite compound, has b. p. 110—111°/10 mm., D^{15} 0·9846, n_D 1·48905. Reduction of the aldehyde leads to the formation of *d*-tricyclo*eksantalol*, $C_{11}H_{18}O$, b. p. 129—131°/10 mm., D^{18} 0·989, n_D 1·4962, α_D +7°. The oxime of the aldehyde, $C_{11}H_{16}\colon NOH$, b. p. 149—151°/9 mm., D^{15} 1·024, n_D 1·5097, α_D +6°30′, is converted by acetic anhydride into *tricyclo*eksantalonitrile, b. p. 124—128°/10 mm., D^{15} 0·9904, n_D 1·48809, α_D +14°15′ (100 mm. tube), which on reduction with sodium and alcohol yields the *tricyclo*eksantalylamine, $C_{11}H_{17}\cdot NH_2$, b. p. 110—112°/8 mm., D^{15} 0·9409, n_D 1·4915.

*tricyclo*Eksantalic acid, $C_{11}H_{16}O_2$, b. p. 163—165°/9·5 mm., D^{15} 1·0482, n_D 1·49383, α_D +7° (100 mm. tube). The lactone, $C_{11}H_{16}O_2$, m. p. 98—100°, remains unchanged when treated with sodium and alcohol.

Methylhydrochloro*dicyclo*eksantalate, b. p. 154—158°/10 mm., D^{15} 1·103, n_D 1·49668, α_D +16°. *dicyclo*Eksantalic acid has b. p. 168—169°/10·5 mm., D^{15} 1·058, n_D 1·50327. Dihydroeksantalol, $C_{11}H_{20}O$, b. p. 134—136°/10 mm., D^{15} 0·9692, n_D 1·49192, is best prepared by reduction of methyl hydrochloro*dicyclo*eksantalate with sodium and alcohol, and, on treatment with phosphorus pentachloride in light petroleum solution, yields *dihydroeksantalyl chloride*, $C_{10}H_{17}\cdot CH_2Cl$, b. p. 120—123°/10 mm., D^{15} 0·9949, n_D 1·48519, which is converted by sodium and alcohol into *dihydro*dicyclo*eksantalane*, $C_{10}H_{17}Me$, b. p. 75—77°/10 mm. or 204°/768 mm., D^{15} 0·8705, n_D 1·47151. This may be identical with a hydrocarbon obtained by heating *tricyclo*eksantalic acid with hydriodic acid and red phosphorus.

The molecular refractions of *tricyclo*santalaldehyde and its derivatives show a marked increment over the calculated refractions.

G. Y.

***iso*Terpenes of Flawitzky.** EDWARD KREMERS (*Pharm. Rev.*, 1908, **26**, 102—106).—From the *d*- and *l*-pinenes, obtained respectively from Russian and French oil of turpentine, Flawitzky (Abstr., 1880, 264, 402; 1887, 968) prepared certain *iso*terpenes. The method employed involved the hydration of the pinene with dilute alcoholic sulphuric acid, and subsequent dehydration by means of acetic anhydride. Flawitzky was of opinion that these hydrocarbons were identical with the limonenes, and that their production was accompanied by the formation of considerable quantities of dipentene. These conclusions have now been confirmed. E. G.

Optical Rotation of Spirits of Turpentine. CHARLES H. HERTY (*J. Amer. Chem. Soc.*, 1908, **30**, 863—867).—The dextrorotatory character of American oil of turpentine has been shown by Long to be due to the fact that its chief constituent is the dextrorotatory oil of *Pinus palustris.*

A study has been made of the oils of *Pinus palustris* (the "long leaf pine") and *P. heterophylla* (the "Cuban" or "slash pine"). Specimens of the oleo-resins were collected from trees of different ages and tapped to different depths. The rotatory power of the volatile oils distilled from these specimens showed a wide variation, even among those obtained from the same species, and sometimes among those obtained from the same tree at different ages. In general, the results confirm Long's observation that the volatile oil of *P. palustris* is dextro-, and that of *P. heterophylla* is lævo-, rotatory, but this is not invariably true. These oils consist largely of mixtures of *d*- and *l*-pinene, the preponderance of one or the other determining the character of the rotatory power. E. G.

Semicatalysis : Oxidation of Hydrocarbons by Air in the Presence of Phosphorus. ALBERT COLSON (*Compt. rend.*, 1908, **146**, 817—818. Compare this vol., ii, 176).—Yellow phosphorus only dissolves in oil of turpentine in the absence of air, and on cooling the solution snow-white crystals are obtained. In the presence of air, the liquid becomes cloudy, and a white, odorous deposit, sometimes curdled and sometimes colloidal, is formed. Since this deposit is not decomposed by water and does not redden litmus, it cannot contain free phosphoric acid, and the fact that it is soluble in dilute ammonia shows the absence of free turpentine. Evaporation of its ethereal solution leaves a resin, m. p. 77—78°, having a camphor-like smell, and a composition corresponding with the formula $(C_{10}H_{16}O_3)_2H_3PO_4$. The degree of oxidation of the turpentine varies with the experimental conditions, but two molecules of the hydrocarbon seem always to react with one atom of phosphorus. The acetic acid solution of this compound is apparently unstable, since its m. p. rises on keeping. The turpentine is certainly oxidised, but, since the product is formed immediately, the phenomenon cannot be described as a slow oxidation, and it is not a case of real catalysis, since the phosphorus enters into the product. The author proposes to call the change, which is also characteristic of benzene, a *semicatalysis.*

E. H.

Volatile Oil of Pinus serotina. CHARLES H. HERTY and W. S. DICKSON (*J. Amer. Chem. Soc.*, 1908, **30**, 872—874).—The volatile oil distilled from the oleo-resin of *Pinus serotina* (the Pond pine) gives the following fractions on re-distillation under the ordinary pressure: at 172—175°, 27·4%, with $[n]^{20}_{D}$ 1·4716 and α_D −87°53′ (100 mm. tube); at 175—180°, 57·0%, with $[n]^{20}_{D}$ 1·4724 and α_D −92°21′ (100 mm. tube); at 180—185°, 8·4%, with $[n]^{20}_{D}$ 1·4744 and α_D −92°14′ (100 mm. tube); above 185°, 7·2%, with $[n]^{20}_{D}$ 1·5045. The fraction of b. p. 175—176° contains a large proportion of limonene.

The resin left after distilling off the oil is pale yellow, and has an acid value 167. E. G.

Constituents of Tarragon Oil (Oleum dracunculi). MAURICE DAUFRESNE (*Chem. Zentr.*, 1908, i, 1057; from *Bul. Sci. Pharm.*, 1908, **15**, 11—20).—A sample of French oil, D^{15} 0·949, $\alpha+7°8'$, $n_D^{19\cdot5}$ 1·51695, and a German oil, D^{15} 0·945, $\alpha+7°24'$, n_D^{15} 1·51645, have been examined and found to contain 15—20% of a terpene, $C_{10}H_{16}$, b. p. 173—175° or 68—70°/13 mm., D^0 0·825, D^{15} 0·812, n_D 1·48636, with a strong smelling hydrocarbon similar to phellandrene, 60—75% of estragole absolutely free from anethole, 0·5—0·6% of *p*-methoxycinnamaldehyde, and 5—20% of higher boiling products. A sample of oil ten years old contained 4·5% of *p*-methoxycinnamaldehyde.

J. V. E.

Ozonides from African Caoutchouc. KURT OTTO GOTTLOB (*Chem. Zentr.*, 1908, i, 467—468; from *Gummi Zeit.*, 1907, **22**, 305—308. Compare Abstr., 1905, i, 364).—Harries' view (Abstr., 1906, i, 30) that the ozonide of gutta-percha is stereoisomeric with that of Para-caoutchouc is criticised. From studying the decomposition of the ozonides of various African caoutchoucs, the conclusion is drawn that African caoutchouc and gutta-percha are undoubtedly related substances; the behaviour of the ozonides allows of a discrimination between Para-caoutchouc and African caoutchouc.

J. V. E.

Manila and Pontianac Copals. CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1908, [iv], **3**, 453—459. Compare Abstr., 1907, i, 67).—Manila "hard" copal has D^{17} 1·065, m. p. 190°, acid number 72·8, and Köttstorfer number 87. Manila "friable" copal has D^{17} 1·060, m. p. 120°, acid number 145·2, and Köttstorfer number 185·1.

Pontianic copal has D^{16} 1·037, m. p. 135°, acid number 134·3, and Köttstorfer number 186·5.

The solubilities of these three copals in twelve common organic solvents are tabulated in the original. T. A. H.

Burseracin and its Effects. WERNER VON BOLTON (*Zeitsch. Elektrochem.*, 1908, **14**, 211—216).—Myrrh was used by the ancients for embalming and healing wounds. The active substance is isolated by extracting with alcohol, evaporating to dryness, and then extracting with water. The substance so obtained, *burseracin*, forms 1·5 to 2% of the original myrrh; after purification by solution in ether, it is a yellow, hygroscopic powder, m. p. 78·15°, readily soluble in hot water. It reduces Fehling's solution, and yields a hydrazone. An analysis and molecular weight determination point to the formula $C_{20}H_{28}O_8$. It is not a glucoside. Its odour and taste resemble those of burnt sugar, and it is also very bitter. It is oxidised by potassium permanganate. It leaves 2·69 to 3·06% of ash, consisting of calcium oxide. When evaporated over a flame with hydrogen peroxide, it explodes violently; by evaporation in a vacuum, a glassy, hygroscopic mass is obtained, which softens at 52°, fuses completely at 100°, and explodes on further heating. It liberates iodine from potassium iodide; titanic acid does not give the reaction of hydrogen peroxide. This substance is named *oxyburseracin*. It seems to give off β-rays and also γ-radia-

tion, as indicated by the discharge of an electroscope. It appears therefore to be an artificial radioactive substance. Neither burseracin nor oxyburseracin is poisonous; the latter coagulates fresh blood; the coagulum, filtered off and dried, forms an elastic membrane; no coagulum is formed in absence of air; burseracin has these properties in a less degree.
T. E.

Japanese Lacquer. Kisaburō Miyama (*J. Coll. Eng. Tokyo*, 1908, **4**, 89—110).—The principal constituent does not contain nitrogen, as supposed by Tschirch and Stevens (Abstr., 1906, i, 31), and is a catechol derivative of the probable composition $C_{34}H_{50}O_4$; the name *urushiol* is now suggested. It is a liquid which cannot be distilled; in the presence of lead oxide, manganese dioxide, &c., it hardens, even when the oxydase (laccase) is absent; it also hardens in the absence of any oxidising agent when heated above 96°. Urushiol gives a green coloration with ferric chloride, and reduces ammoniacal silver solution, but not Fehling's solution. It yields a tetra-acetyl and a tetrabenzoyl derivative, and readily absorbs 8 atoms of bromine; with excess of bromine, a substitution product, $C_{34}H_{42}Br_{12}(OH)_4$, is formed. The best raw lacquer contains about 80—87% of urushiol, 9—12% of moisture, a few per cent. of gum, and rather more than 1% of nitrogenous substances, but inferior (Chinese and Indian) varieties may contain very much less urushiol. The (fermentative) drying at the ordinary temperature consists entirely in the absorption of oxygen, but by drying at a high temperature a partial decomposition takes place. Methods for the analysis of lacquer and for the estimation of urushiol (by precipitation as the barium compound) are described.
G. B.

Decomposition of Amygdalin by Emulsin. Karl Feist (*Arch. Pharm.*, 1908, **246**, 206—209. Compare Caldwell and Courtauld, Trans., 1907, **91**, 666, 671; Auld, Proc., 1907, **23**, 72; 1908, **24**, 97).—The benzaldehydecyanohydrin, formed when amygdalin is decomposed by emulsin at the atmospheric temperature, is a mixture of the racemic and dextro-rotatory forms, and on steam distillation becomes entirely racemised, so that commercial bitter almond oil is always optically inactive. On hydrolysis, the mixture of the *r*- and *d*-forms of the cyanohydrin yields a mixture of *r*- and *l*-forms of mandelic acid. *d*-Benzaldehydecyanohydrin probably has $[\alpha]_D$ +112°. It is suggested that by the action of emulsin at low temperatures on prulaurasin, *r*-benzaldehydecyanohydrin could be obtained, and that the lævo-form could be prepared in like manner from sambunigrin.
T. A. H.

Rhamnosides. Ernst Schmidt (*Arch. Pharm.*, 1908, **246**, 214—224. Compare Abstr., 1904, i, 681).—The author, in conjunction with collaborators, has shown (*loc. cit.*) that sophorin and caper-rutin are identical, and globularia-citrin (Abstr., 1903, ii, 608) possibly identical with rutin. The present paper deals with viola-rutin (viola-quercitrin), fagopyrum-rutin, globularia-citrin, and caper-rutin, and shows that the first three are also identical with rutin. The identity of caper-rutin with rutin is still undecided, since it has been found impossible so far to reconcile a slight difference in melting point between the two substances, but this may be due to traces of impurity in the caper-rutin used. It is shown that viola-rutin, on decomposition by acids, yields 1 mol. each of quercetin, rhamnose, and dextrose, and not, as A. G. Perkin supposed (Trans., 1902, 81, 478), 2 mols. of dextrose, whence it becomes probable that osyritrin and myrticolorin, which Perkin (*loc. cit.*) showed were identical with viola-rutin, are identical with rutin. Rutin crystallises with $3H_2O$, and loses 1 mol. of water slowly at temperatures above 20° and rapidly at 100°, and the remaining 2 mols. at 115°.

T. A. H.

Viola-rutin (Viola-quercitrin). AEMILIUS WUNDERLICH (*Arch. Pharm.*, 1908, **246**, 224—238. Compare preceding abstract).—A detailed account of the isolation of viola-quercitrin from the flowers of *Viola tricolor*, and of the comparison of this glucoside with rutin, is given, resulting in the proof that the two are identical. The flowers also contain salicylic acid, a trace of alkaloid, and a second colouring matter, which is soluble in water, and gives with hydrochloric acid violet, with dilute alkali solutions blue, and concentrated alkali solutions green, colorations.

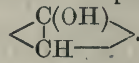
T. A. H.

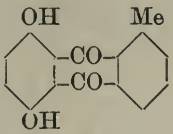
Euphorbone. OSKAR EMMERLING (*Ber.*, 1908, **41**, 1373—1378. Compare Paul, *Diss.*, *Berlin*, 1905).—Euphorbone, $C_{30}H_{48}O$, has m. p. 115—116°, $[\alpha]_D^{15}$ +16·46°. With benzoic anhydride at 160°, it yields a *benzoyl* derivative, $C_{30}H_{47}\cdot O\cdot COPh$, m. p. 128—130°, which is also formed by the action of benzoyl chloride in the presence of pyridine. The p-*nitrobenzoyl* derivative has m. p. 140°.

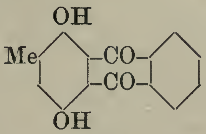
The compound combines with bromine vapour, yielding the unstable compound $C_{30}H_{48}OBr_8$, which begins to decompose at 135°. When crystallised from alcohol, it yields the compound $C_{30}H_{48}OBr_4$, m. p. 83°. When boiled with concentrated nitric acid, euphorbone yields a small amount of ββ-dinitropropane. It is not oxidised by hypobromite.

J. J. S.

Compounds from Rhubarb and Allied Substances. OSWALD HESSE (*J. pr. Chem.*, 1908, [ii], **77**, 383—390. Compare this vol., ii, 418).—A number of errors in the previous paper under the same title (Abstr., 1900, i, 40) are now corrected.

Jowett and Potter's statement (Trans., 1902, 81, 1578) that chrysophanohydroanthrone, the reduction product of chrysophanic acid, is identical with chrysarobin is confirmed. The name chrysophananthranol is preferred for this substance, as it contains the grouping  $<\begin{array}{l}\mathrm{C(OH)}\\ \;| \\ \mathrm{CH}\end{array}>$. Chrysophanic acid has probably the constitution (I), as it gives Bornträger's reaction, as do also emodin, alemodin (aloe-emodin), rhabarberone, physcione, chrysarone, and rhein, whilst methylquinizarin, which does not give this reaction, is considered to have the constitution (II) (compare Liebermann, Abstr., 1900, i, 355; Tschirch and Christofetti, Abstr., 1905, ii, 851).


(I.)


(II.)

Emodin remains unchanged when treated with chromic acid in acetic acid solution, but on reduction with hydriodic acid yields *emodinanthranol*, $C_{15}H_{12}O_4$, which crystallises in light yellow leaflets, m. p. 236°, and gives a brownish-red coloration with alcoholic ferric chloride. The same anthranol is obtained from emodin from rhubarb and from that from *Rhamnus Frangula.*

Reduction of aloe-emodin, m. p. 223—224°, with hydriodic acid leads to the formation of a *product*, $C_{15}H_{12}O_3$, m. p. 182°, which gives an olive-green coloration with ferric chloride in alcoholic solution, and may be identical with Oesterle's substance obtained by reduction of aloe-emodin with tin and hydrochloric acid (Abstr., 1900, i, 304).

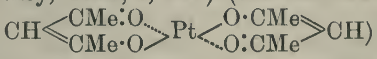
Rhein, $C_{15}H_{10}O_6$, has m. p. 312—316° (sublimes); the m. p. 262—265° (Abstr., 1900, i, 40) is that of the monoacetyl-derivative. The diacetyl derivative, m. p. 240° (compare Tschirch and Heuberger, Abstr., 1903, i, 107; Tschirch and Edner, Abstr., 1907, ii, 501), contains two free hydroxyls, as it dissolves in 2 mols. of potassium hydroxide in aqueous solution; it is rapidly hydrolysed by excess of alkali. The *sodium* and *potassium*, $C_{15}H_8O_6K_2$, derivatives of rhein are described. When boiled with hydriodic acid, D 1·7, rhein forms a dark mass, from which it is regained unchanged on treatment with boiling acetic acid or acetic anhydride. G. Y.

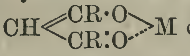
The Chlorophyll Group. Action of Acids on Chlorophyll. LAD. HILDT, LEON MARCHLEWSKI, and J. ROBEL (*Biochem. Zeitsch.*, 1908, 10, 131—166).—Under the name of chlorophyllan, Hoppe-Seyler described a product obtained by the concentration of an alcoholic extract of chlorophyll, the formation of which, as Tschirch subsequently showed, was due to the presence of plant acids. Schunck and Marchlewski, under the name of phyllogen, described a product obtained by treating an alcoholic extract of chlorophyll with gaseous hydrochloric acid. Later still, Willstätter and Hocheder, under the name of phaeophytin, described a product obtained from chlorophyll by treatment with oxalic acid.

The substances described under these names have been further examined, and the authors come to the conclusion that they are identical products with varying quantities of impurities. The chlorophyllan was purified by repeated solution in chloroform and precipitation by alcohol; the product was not entirely soluble in the first-named solvent, and in this way an impurity could be separated. Nor were the products obtained from different plants always identical, for in some cases the ethereal solution, on shaking with 15% hydrochloric acid solution, yielded some colouring matter to the acid. As Schunck and Marchlewski have previously shown, phyllogen, on treatment with acids, yields phylloxanthin and phyllocyanin, of which the latter is soluble in 15% hydrochloric acid and the former only in 24% acid. Some of the preparations, which as originally obtained yielded no colouring matter to 15% hydrochloric acid when the ethereal solution was shaken with acid of this strength, could be made to do so after warming for three hours with ½% oxalic acid solution. Raw chlorophyllan also yields pigment to 5% hydrochloric acid, not, however, the product purified in the manner already described. The conclusions obtained by chemical methods were confirmed by examination of the optical behaviour (absorption spectra) both of the substances themselves and their zinc and copper salts. It is proposed to retain the name chlorophyllan, and to discard the names phyllogen and phaeophytin. S. B. S.

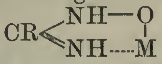
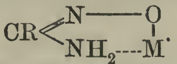
Is Phosphorus an Essential Constituent of Chlorophyllins? M. Tsvett (*Ber. deut. bot. Ges.*, 1908, **26a**, 214—220).—The author agrees with Willstätter (Abstr., 1907, i, 71) that chlorophyll does not contain phosphorus, and attributes the presence of phosphorus in the preparations of Stoklasa, Brdlik, and Just (this vol., i, 279) to contamination with colourless lecithins. This is partly due to these authors having extracted their chlorophyll from the aqueous alcoholic solution with benzene, instead of with light petroleum. Experiments by the author's fractional adsorption method are quoted in support of his views. G. B.

Acid Derivatives of Chlorophyllin. M. Tsvett (*Ber.*, 1908, **41**, 1352—1354. Compare Abstr., 1906, i, 973; ii, 144; 1907, i, 787, 948).—Willstätter and Hocheder's phaeophytin (Abstr., 1907, i, 784) appears to be a mixture of α- and β-chlorophyllans. J. J. S.

Theory of Mordant Dyes. Alfred Werner [with E. Thomann] (*Ber.*, 1908, **41**, 1062—1071).—Liebermann and Kostanecki's rule (Abstr., 1888, 274; 1889, 137, 868) that the oximino- and hydroxyl-groups in compounds which give mordant dyes with basic oxides are in the ortho- or peri-positions, was extended by Möhlau and Steimmig (*Zeitsch. Farb. Text. Chem.*, 1904, **3**, 358), who stated that a hydroxyl in the ortho- or peri-position to a chromophore was requisite for such a dye. Tschugaeff (Abstr., 1907, i, 17, 392, 830), from a study of the α-oximino-ketones, drew the conclusion that the mordant properties are due to metallic derivatives having a cyclic complex structure. These conceptions have been extended, and a general theory arrived at. The internally complex salts of acetylacetone (Werner, Abstr., 1901, i, 682; compare Dilthey, 1906, i, 342) (the formula of the platinum salt is now given as  $\mathrm{CH}<\begin{matrix}\mathrm{CMe{:}O}\cdots\\ \mathrm{CMe{\cdot}O}\end{matrix}>\mathrm{Pt}<\begin{matrix}\mathrm{O{\cdot}CMe}\\ \cdots\mathrm{O{:}CMe}\end{matrix}>\mathrm{CH}$) and the complex salts investigated by Bruni (Abstr., 1904, i, 855) and Ley (Abstr., 1907, i, 301, 302, 730) are all characterised by great stability, sparing solubility in water, and unlikeness to ordinary metallic salts. The varying colour of such salts is held to be due to the nature of the supplementary valencies of the group united to the metal.

The following additional evidence is adduced. The three $\alpha\gamma$-diketones, benzoylacetone, dibenzoylmethane, and anisoylbenzoylmethane give with ferric oxide orange-yellow shades, and the conclusion is drawn that they have the complex  $CH<\begin{matrix}CR\cdot O\\ CR:O\end{matrix}>M$ derived from the enolic form, a view supported by the examination of hydroxymethylenecamphor, which gives violet tones.

α-Benzilmonoxime, moreover, has dyeing properties, whereas the γ-compound has not, a result in agreement with the stereochemical hypothesis, and also pointing to the cyclic complexes being six-membered rings. *iso*Nitrosocamphor has no dyeing property. In addition to β-benzildioxime, dimethylglyoxime and methylethylglyoxime give red and orange-red shades with nickel.

Amino-oximes, such as benzenylamino-oxime and *o*- and *p*-tolenylamino-oximes, give the same tint with a copper salt, whilst oxalenediamino-oxime gives a much more intense colour; their constitution is given as  $CR<\begin{matrix}NH-O\\ NH\cdots M\end{matrix}$ or  $CR<\begin{matrix}N-O\\ NH_2\cdots M\end{matrix}$. The hydroxamic acids show analogous behaviour, and the benzoin of phenylglyoxal,

$$COPh\cdot C(OH):C(OH)\cdot COPh,$$

has marked dyeing properties with mordants.

The conclusion drawn from the above facts is that the mordant dyeing properties of chemical compounds depend on the capacity of forming these co-ordinated cyclic complex salts. Compounds which would not be expected to form these complex salts, such as *o*-hydroxybenzylideneacetophenone, which would form an eight-membered ring, have no dyeing function whatever. W. R.

Theory of Mordant Dyes. CARL LIEBERMANN (*Ber.*, 1908, **41**, 1436—1444).—Polemical. A disputation of Tschugaeff's (Abstr., 1907, i, 392, 830) and of Werner's (preceding abstract) criticisms of the author's metallocyclic theory of the constitution of lakes.
C. S.

The Japanese Dyewood "Doss." E. ITO (*J. Coll. Eng. Tokyo*, 1908, **4**, 57—62).—*Ilex Mertensii* or "Doss" contains a yellow colouring matter, *dossetin*, $C_{15}H_9O_5$, yellow needles from methyl alcohol, m. p. 271—272°; it can be used with a mordant, but has no great tinctorial value. G. B.

Coumarin Derivatives. ALBERT REYCHLER (*Bull. Soc. chim.*, 1908, [iv], **3**, 551—556 *).—Ebert's process (Abstr., 1885, 391) for the conversion of coumarin into coumaric acid gives good results when alcohol free from water is employed (compare von Miller and Kinkelin, *ibid.*, 1889, 989). Methylcoumaric acid was obtained by the action of methyl iodide on coumarin in presence of sodium ethoxide, and saponification of the methyl methylcoumarate first formed. Using methyl sulphate in place of methyl iodide, the reaction proceeds more rapidly, but the yield of acid is smaller. If sufficient water is added to the alcohol used, the isomeride of methylcoumaric acid, methylcoumarinic acid, is obtained (Perkin, Trans., 1881, **39**, 409). The methyl methylcoumarinate, formed as an intermediate product in this reaction, on distillation must be partly converted into methyl methylcoumarate, since the distillate on saponification yields some methylcoumaric acid, although the latter is not formed by the action of alcoholic sodium hydroxide on methylcoumarinic acid.

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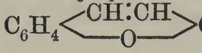
* and *Bull. Soc. chim. Belg.*, 1908, **22**, 177—180.

Since salicylic acid boils at 196° and its ethyl ether at 238°, it seems probable that the former has the ketonic-aldehyde structure, whilst the latter is a true phenol ether. Tiemann and Herzfeld's conversion of salicylaldehyde into acetylcoumaric acid (Abstr., 1877, i, 708), which may be transformed into coumaric acid and eventually coumarin, is explained by assigning the following formulæ to the last three substances:

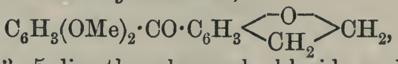
$OAc{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H \longrightarrow OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H \longrightarrow$



$C_6H_4{<}\begin{smallmatrix}CH{:}CH\\ O\end{smallmatrix}{>}CO$, and assuming a *cis-trans* change to occur during the transformation; a similar explanation accounts for Perkin's synthesis of coumarin and for von Miller's conversion of *o*-nitrosalicylaldehyde into the corresponding nitrocoumarin (*loc. cit.*). When the phenolic hydrogen of salicylaldehyde is replaced by an alkyl group, there is less tendency to dehydration, and consequently less tendency to form coumarin derivatives (von Miller, *loc. cit.*). T. A. H.

Elimination of the Methoxy-group. Stanislaus von Kostanecki and Victor Lampe (*Ber.*, 1908, **41**, 1327—1329).—It was hoped to obtain by the reduction of leucotrimethylgalloylcoumaran (Abstr., 1907, i, 951) an analogous product to that obtained on the reduction of catechin tetramethyl ether (Abstr., 1907, i, 334). The coumaran ring is, however, very stable, a compound crystallising from dilute alcohol in long leaflets, m. p. 84—85°, and insoluble in alkali, being obtained instead, which is a dimethoxybenzylcoumaran. By the following synthesis of this compound, it has been proved that the methoxy-group in the para-position to the secondary carbinol group has been eliminated during the reduction.

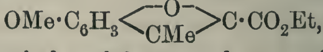
4-*Benzoyl*-3′ : 5′-*dimethoxycoumaran*,



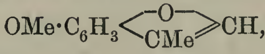
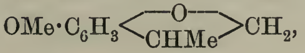
$$C_6H_3(OMe)_2{\cdot}CO{\cdot}C_6H_3{<}\begin{smallmatrix}O\\ CH_2\end{smallmatrix}{>}CH_2,$$

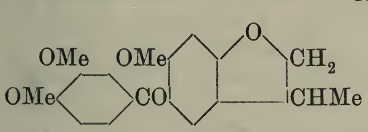
obtained from 3 : 5-dimethoxybenzoyl chloride and coumaran, crystallises from dilute alcohol in short needles, m. p. 94—95°, and on reduction with sodium and alcohol gives a 3′ : 5′-*dimethoxy*-4-*benzylcoumaran*, $C_7H_{18}O_3$, identical in all respects with the product obtained from leucotrimethoxygalloylcoumaran. W. R.

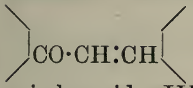
Studies in the Coumaran Group. I. Stanislaus von Kostanecki and Victor Lampe (*Ber.*, 1908, **41**, 1330—1335).—

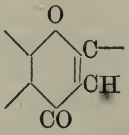


Ethyl 5-*methoxy*-2-*methylcoumarilate*, $OMe{\cdot}C_6H_3{<}\begin{smallmatrix}O\\ CMe\end{smallmatrix}{>}C{\cdot}CO_2Et$, is prepared by adding quickly hot methyl sulphate and potassium hydroxide to a boiling solution of ethyl 5-hydroxy-2-methylcoumarilate (Hantzsch, Abstr., 1887, 282) in alcohol. It is found, in general, that the more energetically the methylation is carried out the better the yield of ether. It crystallises in short, stout needles, m. p. 74—75°. The alkaline filtrate, on acidification, gives 5-*methoxy*-2-*methylcoumarilic acid*, which is also easily obtained by hydrolysing the ester with potassium hydroxide; it separates from dilute alcohol in white needles, m. p. 190° (decomp.). *Methyl* 5-*methoxy*-2-*methylcoumarilate*, $C_{12}H_{12}O_4$, crystallises in needle aggregates, m. p. 78°.

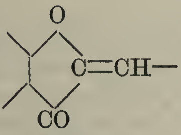
When the methoxymethylcoumarilic acid is heated in a retort, carbon dioxide is evolved, and a mixture of unchanged acid and 5-*methoxy*-2-*methylcoumarone*,  $OMe\cdot C_6H_3{<}\overset{-O-}{\underset{CMe}{}}{\gg}CH$, distils over, and are separated by distillation with steam, in which the latter is volatile. The coumarone crystallises in white leaflets, m. p. 58°, b. p. 246°/705 mm., and has an odour resembling that of absinthe. On its repeated reduction in alcoholic solution with sodium, 5-*methoxy*-2-*methylcoumaran*,  $OMe\cdot C_6H_3{<}\overset{-O-}{\underset{CHMe}{}}{>}CH_2$, is obtained as a colourless oil, b. p. 245°/705 mm., and this, on treatment with veratroyl chloride and aluminium chloride in carbon disulphide, leads to the formation of 4-*veratroyl*-5-*methoxy*-2-*methylcoumaran*, annexed formula, which separates from dilute alcohol in needle aggregates, m. p. 119—120°. The *leuco*-compound has only as yet been obtained as a viscid, colourless oil. W. R.



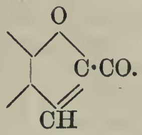
Function of the Double Chromophore CO·C:C. Felicia Zwayer and Stanislaus von Kostanecki (*Ber.*, 1908, 41, 1335—1341).—Dyes with the double chromophore CO·C:C may be divided in four classes, according to the position of the chromophores, thus: (1) the two chromophores "cyclostatic," as in hydroxyflavone, I; (2) the two chromophores "streptostatic," as in hydroxychalkone,  $CO\cdot CH{:}CH$; (3) "CO cyclostatic," "C:C streptostatic," as in oxindogenide, III; (4) "CO streptostatic," "C:C cyclostatic," as in hydroxy-1-benzoylcoumarone, IV.



(I.)



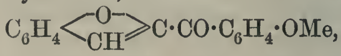
(III.)



(IV.)

The first class are characterised by their yellow colour and colourless alkyl and acyl derivatives, the second are reddish-yellow, and their alkyl and acyl derivatives are yellow. The colours of the third class are closely related to those of the second class (Klobski and Kostanecki, Abstr., 1898, i, 371), and both contain "C:C streptostatic." Representatives of the fourth class had not hitherto been prepared, and, as it was of importance from the standpoint of colour that they should be obtained, the investigation was undertaken.

2-*Hydroxy*-4′-*methoxychalkone*, $OH\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot C_6H_4\cdot OMe$, prepared by condensing salicylaldehyde and *p*-methoxyacetophenone in the presence of 50% sodium hydroxide, crystallises in yellow leaflets, m. p. 148° (decomp.). The *sodium* salt is orange-red and easily soluble, the *acetate*, $C_{18}H_{16}O_4$, crystallises in pale yellow leaflets, m. p. 129—130°. When the acetate is treated with 1 mol. of bromine, 2-*acetoxy*-4′-*methoxychalkone dibromide*, $C_{18}H_{16}O_4Br_2$, is formed, which separates from alcohol in white needles, m. p. 123°. This, on treatment with alcoholic potassium hydroxide, leads to the formation of 1-p-*methoxybenzoylcoumarone*,

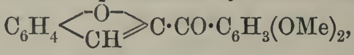


$C_6H_4{<}\substack{O\\CH}{>}C\cdot CO\cdot C_6H_4\cdot OMe$,

which crystallises in white needles, m. p. 103—104°. The same compound is obtained from coumarilic chloride, anisole, and aluminium chloride.

1-p-*Hydroxybenzoylcoumarone*, $C_{15}H_{10}O_3$, prepared from coumarilic chloride, phenol, and aluminium chloride, and hydrolysis of the resulting coumarilic ester by alkali, crystallises from dilute alcohol in short, stout, light yellow needles, m. p. 179—180°. It is therefore more similar in colour to 4-hydroxychalkone (Bablich and Kostanecki, Abstr., 1896, i, 239) and to 4′-hydroxychalkone (Abstr., 1899, i, 704) than to 4′-hydroxyflavone (Abstr., 1900, i, 669). The *acetate*, $C_{17}H_{12}O_4$, forms white needles, m. p. 116—117°.

[With Frl. M. Szwejkowska.]—2-*Hydroxy*-3′ : 4′-*dimethoxychalkone*, $OH\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_3(OMe)_2$, obtained by the condensation of salicylaldehyde with acetoveratrone, forms stout, yellow prisms, m. p. 148°. Its *sodium* salt is red. 2-*Acetoxy*-3′ : 4′-*dimethoxychalkone dibromide*, $C_{19}H_{18}O_5Br_2$, forms white needles, m. p. 174—175° (decomp.), and is converted by alcoholic potassium hydroxide into 3′ : 4′-*dimethoxy*-1-*benzoylcoumarone*,



$C_6H_4{<}\substack{O\\CH}{>}C\cdot CO\cdot C_6H_3(OMe)_2$,

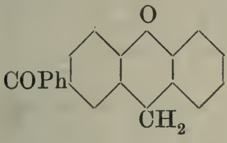
which may also be obtained from veratrole and coumarilic chloride. It forms colourless, well-defined rhombohedra, m. p. 90—91°.

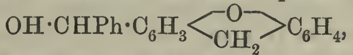
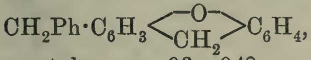
All the compounds described give characteristic colorations with sulphuric acid.

As benzoylphenylacetylene is colourless, the conclusion that all chromophores contain double linkings is strengthened. W. R.

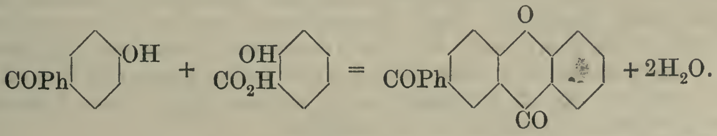
Coumaroneglycol. Johannes Boes (*Chem. Zentr.*, 1908, i, 1185; from *Apoth. Zeit.*, 1908, **23**, 153).—The action of hypochlorous acid on coumarone gives rise probably to a mixture of isomeric coumarone chlorohydrins; the product, however, when purified from benzene yields a *coumarone chlorohydrin*, which crystallises in needles, m. p. 123°. This substance, when decomposed in alcoholic solution by means of potassium hydroxide, neutralised with acetic acid, and steam distilled, gives a small quantity of *coumaroneglycol*, m. p. 151°, which crystallises from benzene. No glycol could be obtained by the oxidation of coumarone by means of potassium permanganate or bleaching powder. J. V. E.

Action of Benzoyl Chloride on Xanthen. J. Heller and Stanislaus von Kostanecki (*Ber.*, 1908, **41**, 1324—1327).—The conclusion previously drawn that the benzoylcoumaran and benzoylchroman, prepared by the action of the acyl chloride on the cyclic phenol ether in the presence of aluminium chloride, are para-derivatives was not directly proved, because the rupture of the oxygen ring did not take place (Abstr., 1907, i, 950). In order to support this conclusion, the action of the acyl chloride on xanthen has been studied, and, as it is proved directly that substitution occurs in the para-position in this case, the conclusion with regard to the coumaran and chroman derivatives is regarded as resting on a solid basis.



2-*Benzoylxanthen*, annexed formula, prepared by shaking xanthen, benzoyl chloride, and aluminium chloride in carbon disulphide solution and afterwards leaving it for forty-eight hours, crystallises from a mixture of pyridine and alcohol in white leaflets, m. p. 148°. By reduction of an alcoholic solution with zinc dust and potassium hydroxide, *leuco-2-benzoylxanthen*,  $OH\cdot CHPh\cdot C_6H_3<\genfrac{}{}{0pt}{}{O}{CH_2}>C_6H_4$, is obtained, which crystallises in stout prisms, m. p. 136—137°. Reduction, however, of the benzoyl compound or its leuco-derivative with sodium and alcohol leads to the formation of 2-*benzylxanthen*,  $CH_2Ph\cdot C_6H_3<\genfrac{}{}{0pt}{}{O}{CH_2}>C_6H_4$, which separates from alcohol in white crystals, m. p. 93—94°.

Oxidation of 2-benzoylxanthen with boiling nitric acid leads to the formation of 2-*benzoylxanthone*, $C_{20}H_{12}O_3$, which crystallises from alcohol in glistening plates, m. p. 146—147°. The constitution of this compound is proved by its preparation from *p*-hydroxybenzophenone and salicylic acid in the presence of acetic anhydride:



W. R.

Tritan Series. Hans von Liebig (*Annalen*, 1908, **360**, 128—264).—*Fluorescence and Colour of Organic Substances.*—Whilst many organic substances are coloured and fluorescent, the phenomenon of pleochroism is less common, and all three properties have been observed previously in only one substance, chlorophyll, which in solution has a red fluorescence, and appears green in thin layers, but in thicker layers is green by reflected, red by transmitted, light. The vegetable dyes belong to the aromatic series, and contain commonly two hydroxyls in the meta-position to each other. The frequency with which such dyes occur suggests that they are related to chlorophyll, the more that *m*-dihydroxy-compounds are especially suited for the assimilation of carbon dioxide and oxygen. The simplest *m*-dihydroxy-compound, resorcinol, forms fluorescent dyes when heated with dehydrating agents, but the properties of these dyes render them unsuited for the study of the phenomena of colour and fluorescence. On the other hand, many of the dyes formed by condensation of resorcinol with other substances contain a pyrone ring which is itself a chromophore, and therefore disguises the colour and fluorescent properties of the resorcinol grouping. Resorcinol and benzil, however, condense, forming a series of coloured and colourless compounds, the "tritan" (triphenylmethane) derivatives (for the constitution and nomenclature, see Abstr., 1905, i, 781; 1907, i, 45, 930, 1045), which cannot contain a pyrone grouping, and which in consequence of the accumulation of benzene nuclei in the molecule crystallise readily and have convenient solubilities. As the phenyl groups are not chromophoric, the colour and fluorescence of the tritan compounds must be ascribed to the resorcinol portion of the molecule.

Whilst 2 : 4-dihydroxytritanolactone is colourless and not fluorescent, *m*-tetra-2 : 4-dihydrotritanol diether and its diacetyl derivative are colourless, but fluoresce blue, and a tetra-acetyl derivative of the triether is blue, but is not fluorescent. Two of the tritanone ethers are red or brown, and have a weak green fluorescence; the monoacetyl derivative of the diether and the penta-acetyl derivative of the triether are yellow and have a strong green fluorescence. *m*-Di-2 : 4-dihydroxytritanol ether is brown and fluoresces blue in alkaline aqueous, but green in alkaline alcoholic, solution. The solutions of the tritanone-acid-ether derivatives are pleochroic, being blue by reflected, and red by transmitted, light when concentrated, but red only when dilute. Finally, the penta- and hepta-acetyl derivatives of *m*-tetra-2 : 4-dihydroxytritanol ether (EL, p. 447) exhibit not only colour, pleochroism, and fluorescence as does chlorophyll, but also varying fluorescence. Of the tritan compounds, those with one resorcinol group are colourless and not fluorescent, colour and fluorescence appearing when the molecule contains two resorcinol groups, whilst compounds with four resorcinol groups are pleochroic. It is remarkable that these variations in colour properties depend on the building up of arrangements of carbon, oxygen, and hydrogen atoms without the assistance of nitrogen.

These observations are made the basis of a long discussion of the theory of colour and fluorescence of organic compounds, which leads to the following conclusions:

1. The ultraviolet fluorescence of benzene and its most simple derivative arises from oscillations, probably of electrons, caused by the circular shifting of the double linkings of Kekulé's benzene ring.

2. Persistent fluorescence in the visible spectrum is caused by retardation of the oscillation in two ways. Firstly,

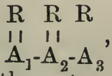
3. by union of the benzene ring with other rings, as in naphthalene and anthracene, which causes usually blue, more seldom yellowish-green, fluorescene; and secondly,

4. by the coupling of the benzene ring with other rings by means of oxygen, sulphur, or nitrogen bridge-atoms, which increases the

intensity and diminishes the rate of the oscillations and causes red, yellow, or green fluorescence.

5. Transient fluorescence may arise from the change of non-benzenoid into benzenoid structures.

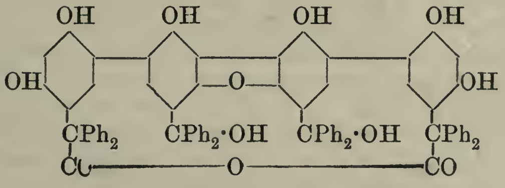
6. True quinones fluoresce in the ultra-violet, and not in the visible spectrum unless benzenoid nuclei are present.

7. There exists only one organic chromophore, the system  $\overset{R}{\overset{\|}{A_1}}\text{-}\overset{R}{\overset{\|}{A_2}}\text{-}\overset{R}{A_3}$, in which three singly-linked atoms are each united to another atom by a double bond.

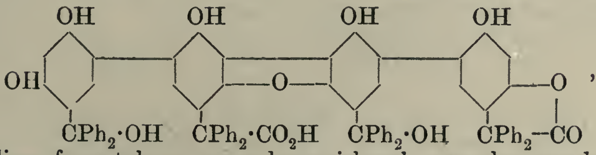
8. This system (7) does not alone suffice to produce colour; there must be present some influence, the nature of the atoms or a cyclic grouping, which causes the three double linkings to assume a given relation to one another.

Derivatives of Tetra-2 : 4-*dihydroxytritanol.*—The product obtained on fusing benzil with resorcinol contains resorcylic acid, benzoic acid, 2 : 4-dihydroxytritanic acid, resorcinolbenzein, and five coloured substances, which for convenience are termed EU, EL, EK, EN, and EB. Tetraphenyldifuran, previously stated to be a product of the reaction, has now been found to have been formed from resorcinol and a small amount of benzoin. Of the five coloured substances, EU (2^{I}-acetoxy-*m*-tetra-2 : 6-dihydroxytritanol-$6^{I}2^{II},6^{III}2^{IV}$-diether-$7^{II}7^{III}$-anhydride) has been already described (Abstr., 1907, i, 45). The present paper contains an account of the method employed in separating the fusion products and of the remaining four coloured substances. When distilled, these decompose, forming diphenylmethane.

EL (m-*tetra*-2 : 4-*dihydroxytritan*-II,III-*ol*-I,IV-*anhydride*-$6^{II}2^{III}$-*ether* or m-*tetra*-2 : 4-*dihydroxytritan*-I,III-*ol*-II-*acid*-IV-*lactone*-$6^{II}2^{III}$-*ether*) :



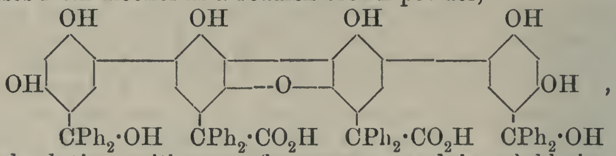
or



crystallises from toluene as a brownish-red, granular powder, m. p. 250—260°, forms red solutions with green fluorescence, and dissolves in aqueous alkalis, separating immediately as the alkaline salts; these form dark bluish-red aqueous solutions with strong green fluorescence. When boiled with alcoholic potassium hydroxide, EL forms m-*tetra*-2 : 4-*dihydroxytritan*-I,IV-*ol*-II,III-*acid*, $C_{78}H_{56}O_{12}$, which is obtained as a brownish-red powder, soluble in aqueous alkali carbonates. The *hydrochloride*, $C_{78}H_{54}O_{12},HCl$, formed by heating

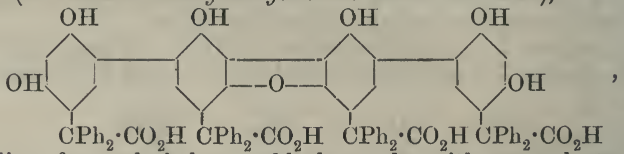
EL with alcoholic hydrogen chloride, is obtained as a brownish-black powder. When heated at 300°, EL loses carbon dioxide and forms a red powder, $C_{76}H_{54}O_8$ or $C_{97}H_{52}O_9$, which is insoluble in alkalis. El-*diacetyl* derivative, $C_{82}H_{58}O_{14}$, m. p. about 140°. The *penta-acetyl* derivative, $C_{88}H_{64}O_{17}$, forms a bluish-red, granular powder, sinters at 170—180°, melts slowly, and decomp. about 200°; the solutions are red with red, or in the presence of ammonia green, fluorescence; by transmitted light, the concentrated solution containing ammonia is green, becoming brown on dilution. The *hepta-acetyl* derivative, $C_{92}H_{70}O_{20}$, a dark red, granular powder, m. p. above 300°, forms similar fluorescent solutions. The *triacetyl* derivative, $C_{84}H_{60}O_{15}$, yellowish-brown powder, m. p. about 210°, is not fluorescent. The colourless *tetra-acetyl*, m. p. about 190°, and *hexa-acetyl*, $C_{90}H_{62}O_{16}$, m. p. about 240°, derivatives are described.

EK (m-*Tetra*-2 : 4-*dihydroxytritan*-II,III-*ol*-I,IV-*acid*-6^{II}2^{III}-*ether*) crystallises from alcohol as a reddish-brown powder,



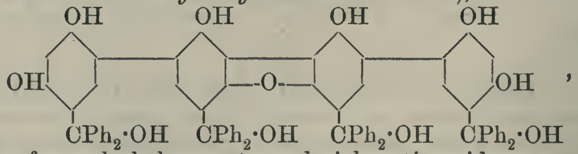
forms red solutions with green fluorescence, and is soluble in alkalis. The *diacetyl*, $C_{82}H_{60}O_{15}$, m. p. 180°, and *penta-acetyl*, $C_{88}H_{64}O_{17}$, m. p. 180—190°, derivatives are not fluorescent.

EN (m-*Tetra*-2 : 4-*dihydroxytritanic acid*-6^{II}2^{III}-*ether*),



crystallises from alcohol as a black powder with green lustre, forms red solutions with green fluorescence, and dissolves readily in cold alkalis. The *triacetyl* derivative, $C_{86}H_{60}O_{17}$, is a brownish-red powder, and forms red solutions, which are not fluorescent. The *tetra-acetyl* derivative, $C_{88}H_{60}O_{17},2C_2H_6O$, is a yellow, granular powder, m. p. 118—125°. The *penta-acetyl* derivative, $C_{90}H_{66}O_{20},2H_2O$, m. p. about 210°, forms solutions with red fluorescence.

EB (m-*Tetra*-2 : 4-*dihydroxytritanol*-6^{II}2^{III}-*ether*),

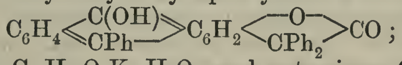


crystallises from alcohol or acetone-glacial acetic acid as a red powder, sinters about 140°, and dissolves in hot aqueous alkalis to a red solution with slight green fluorescence. The *diacetyl* derivative, $C_{80}H_{58}O_{12}$, white powder, sinters at 130°. The *tetra-acetyl* derivative, $C_{84}H_{64}O_{15}$, white powder, m. p. about 125°. The *penta-acetyl* derivative, $C_{86}H_{64}O_{15}$, reddish-brown powder, m. p. about 220°, forms red solutions which are not fluorescent. When heated at 200—220°, EB loses water, forming a *product*, $C_{70}H_{50}O_8$, which is obtained as a red powder, m. p. 180—190°. Reduction of EB with zinc dust and glacial acetic acid leads to the formation of a *product*, $C_{76}H_{54}O_8$, which is obtained as a white powder, m. p. 164—165°.

Combination of Benzil with Phenol.—[With PAUL KEIM.]—Bistrzycki's method of forming tritan derivatives by condensation of benzil with phenols in presence of stannic chloride is not applicable to the formation of resorcinol derivatives, but benzil and resorcinol condense readily when heated alone or with sodium sulphate, or when brought together in cold concentrated sulphuric acid, forming 2 : 4-dihydroxytritanolactone. Whilst 2 : 4-dihydroxydiphenylacetic acid closely resembles triphenylacetic acid, 2 : 4-dihydroxytritanic acid differs markedly in its behaviour, and hence it was thought possible that the condensation product of resorcinol and benzil is 3 : 5-dihydroxytritanolactone. It is now found, however, that 2-hydroxytritanolactone (Abstr., 1907, i, 930, 1045), formed from benzil and phenol, behaves in the same manner as the dihydroxylactone, the constitution of which as 2 : 4-dihydroxytritanolactone is therefore confirmed. *p*-Hydroxytritanolactone is not formed even in traces by the condensation of benzil with phenol. The following details are new.

On hydrolysis with alcoholic potassium hydroxide, methyl *o*-methoxytritanate yields *o*-methoxytritanic acid and a *substance*, $C_{42}H_{38}O_5$, m. p. 106°, which is considered to be a molecular compound of *o*-methoxytritanic acid and *o*-methoxytritanol. A similar molecular compound was previously obtained by hydrolysis of methyl 2 : 4-dimethoxytritanate (Abstr., 1905, i, 781).

The substance, m. p. 239°, formed together with *o*-hydroxytritanolactone by condensation of benzil with phenol (Abstr., 1907, i, 931), is the lactone of diphenyl-2-hydroxy-9-phenylanthranolacetic acid,



$$C_6H_4{<}\begin{matrix}C(OH)\\CPh\end{matrix}{>}C_6H_2{<}\begin{matrix}O\\CPh_2\end{matrix}{>}CO\ ;$$

the *dipotassium*, $C_{34}H_{22}O_4K_2,H_2O$, and potassium, $C_{34}H_{23}O_4K,6H_2O$, salts are described. The lactone is not reduced by zinc dust and glacial acetic acid, but on treatment with chromic acid in glacial acetic acid solution yields a *product*, $C_{34}H_{24}O_5$, which separates from alcohol in colourless crystals, m. p. 148—149°, and gives a greenish-yellow coloration with sulphuric acid. The *dimethyl* derivative,

$$C_{34}H_{22}O_2(OMe)_2,$$

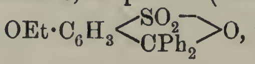
formed by the action of methyl sulphate on the dipotassium salt, crystallises in white needles, m. p. 187°, and remains unchanged when boiled with alcoholic potassium hydroxide. The *trinitro*-compound, $C_{34}H_{19}O_3(NO_2)_3$, forms a yellow powder, m. p. 120—130°.

2 : 4-*Dihydroxytritanolactonesulphonic Acid.*—[With OTTO HERB.]—*o*-Hydroxytritanolactone, *p*-hydroxytritanic acid, and 2 : 4-dihydroxytritanolactone ether do not form sulphonic acids. On the other hand, 2 : 4-dihydroxytritanolactone and its methyl ether, methyl 4-hydroxy-2-methoxytritanate-4-ether, $O[C_6H_3(OMe)\cdot CPh_2\cdot CO_2Me]_2$, 2 : 4-dimethoxytritanic acid and its methyl ester, and *o*-methoxytritanic acid readily form sulphonic acids when shaken with cold concentrated sulphuric acid. The ethoxy-derivatives react even more easily than do

the methoxy-compounds. The carbmethoxy-group, $\cdot CO_2Me$, is split off in the sulphonation of the methyl esters. The 2 : 4-dimethoxytritanolsulphonic acid, formed in this manner from methyl 2 : 4-dimethoxytritanate, is isomeric with that prepared directly from 2 : 4-dimethoxytritanol. 2-Hydroxy-4-acetoxytritanolactone is also readily sulphonated ; the reaction takes place most easily with the tetramethyl ether of 2 : 4-dihydroxytritanolactone ether, which forms a tetrasulphonic acid, whereas the other compounds form monosulphonic acids only.

2-*Hydroxy-4-methoxytritanolactone-5-sulphonic acid*,

$$C_{21}H_{15}O_3\cdot SO_3H,3H_2O,$$

crystallises in needles, m. p. 160—161° ; the *ammonium* salt crystallises in leaflets. The corresponding 4-*ethoxysulphonic acid* ($3H_2O$) forms needles, m. p. 140—141°, and yields a colourless ferric salt which gradually becomes red. 2 : 4-*Dimethoxytritanol-5-sulphonic acid*, $C_{21}H_{19}O_3\cdot SO_3H$, crystallises in needles, m. p. 207—208°, becoming red, decomp. about 330°. The isomeric 6-*sulphonic acid*, leaflets, m. p. 221°, gives a violet coloration with ferric chloride. 2 : 4-*Dimethoxytritanolether-tetrasulphonic acid*, $O[C_6H(OMe)(SO_3H)_2\cdot CPh_2\cdot OH]_2$, gives a green fluorescence with an excess of alkali, but not a coloration with ferric chloride ; the *ammonium* salt, needles. *Ammonium* o-*methoxytritanol-3-sulphonate*, m. p. 180° (decomp.). o-*Ethoxytritanol-6-sulphonic anhydride*,  $OEt\cdot C_6H_3{<}{\scriptstyle\begin{matrix}SO_2-\\CPh_2\end{matrix}}{>}O$, forms colourless needles, m. p. 100° (decomp.).

2 : 4-*Dihydroxytritanolactonesulphonic acid*, $C_{20}H_{13}O_3\cdot SO_3H,2H_2O$, crystallises from benzene in rectangular prisms, m. p. 132°, decomp. about 180°, gives a reddish-violet coloration with ferric chloride, and liberates mineral acids, including sulphuric acid, from their salts. Eighteen salts of this acid are described. The acid remains unchanged when fused with potassium hydroxide or boiled with alcoholic potassium hydroxide in a reflux apparatus. On treatment with acetyl chloride, the monoammonium salt yields *ammonium* 2-*hydroxy-4-acetoxytritanolactonesulphonate*, $C_{22}H_{15}O_4\cdot SO_3NH_4$, needles, m. p. 235—236°, and *ammonium 2-hydroxy-4-acetoxysulphotritanate*, leaflets, m. p. 233° if slowly, or 200—230° if quickly, heated. The *product*, $C_{22}H_{17}O_5\cdot SO_3NH_4$, obtained on successive treatment of 2-hydroxy-4-acetoxytritanolactone with sulphuric acid and ammonium sulphate, crystallises in leaflets, m. p. 235—236°. *Sodium 2-hydroxy-4-acetoxytritanolactonesulphonate*, $C_{22}H_{15}O_4\cdot SO_3Na$, m. p. 124—125°.

2 : 4-*Dihydroxytritanol-5-sulphonic acid*, $C_{19}H_{15}O_3\cdot SO_3H,H_2O$, formed by oxidation of the lactonesulphonic acid, separates from ether in colourless crystals, m. p. 186°.

The sulphonic acid group is split off from 2 : 4-dihydroxytritanolactonesulphonic acid by the action of acetyl chloride on the monoammonium salt or of methyl sulphate on the potassium salt, 2 : 4-dihydroxytritanolactone being formed. In presence of potassium hydroxide, the action of methyl sulphate leads to the formation of methyl 2 : 4-dimethoxytritanate, 2 : 4-dimethoxytritanic acid, and 2-hydroxy-4-methoxytritanolactone. When treated with bromine in glacial acetic acid solution, the sodium sulphonate is converted into Kohlhaas's *bromo*-compound, m. p. 184° (*Diss.*, Marburg, 1905).

The action of nitric acid on the potassium sulphonate in glacial acetic acid solution leads to the formation of *nitro-2 : 4-dihydroxytritanolactone*, m. p. 183°, which forms an *acetyl* derivative, m. p. 159°. *Dinitro-2 : 4-dihydroxytritanol*, yellow crystals, m. p. 175—176°, is formed by the action of concentrated nitric acid on 2 : 4-dihydroxytritanolactone or its potassium sulphonate. On reduction with tin and hydrochloric acid in glacial acetic acid solution, it yields the *diamino*-compound, crystallising in blue leaflets, m. p. 200°.

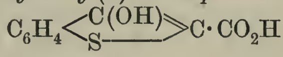
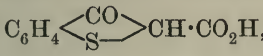
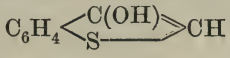
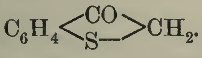
Ferric 2 : 4-dihydroxytritanolactonesulphonate,

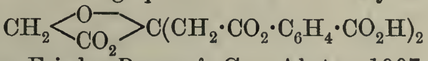
$$(C_{20}H_{13}O_3\cdot SO_3)_3Fe,6H_2O,$$

forms colourless leaflets, which become blue, but retain the same composition on treatment with oxygen in cold ethereal solution. When heated, the blue crystals commence to decompose at 180°, evolving carbon monoxide. When treated with oxygen in aqueous solution, the ferric sulphonate yields a yellow *precipitate*,

$$[(C_{20}H_{13}O_3\cdot SO_3)_2Fe]_2,12H_2O,$$

and a free sulphonic acid. G. Y.

[Preparation of 3-Hydroxy-(1)-thionaphthen-2-carboxylic Acid.] KALLE & Co. (D.R.-P. 192075).—*Carbmethoxy-o-thiobenzoic acid*, $CO_2H\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$, yellowish-white crystals, m. p. 213°, is produced by condensing chloroacetic and thiosalicylic acids or their esters in alkaline solutions. *3-Hydroxy-(1)-thionaphthen-2-carboxylic acid* (*thioindoxylcarboxylic acid*),  $C_6H_4<^{C(OH)}_{S}>C\cdot CO_2H$ or  $C_6H_4<^{CO}_{S}>CH\cdot CO_2H$, is produced together with 3-hydroxy-(1)-thionaphthen by heating the preceding acid with sodium hydroxide and water at 170—200° and acidifying the fusion with dilute mineral acid. When distilled in steam, the carboxylic acid loses carbon dioxide and furnishes 3-hydroxy-(1)-thionaphthen,  $C_6H_4<^{C(OH)}_{S}>CH$ or  $C_6H_4<^{CO}_{S}>CH_2$. G. T. M.

Quinine Salts of Anhydromethylenecitrylsalicylic Acid. LUIGI SANTI (*Boll. chim. farm.*, 1908, **47**, 219—224).—The author has prepared the two following quinine salts of anhydromethylenecitrylsalicylic acid,  $CH_2<^{O—}_{CO_2}>C(CH_2\cdot CO_2\cdot C_6H_4\cdot CO_2H)_2$ (compare Farbenfabriken vorm. Friedr. Bayer & Co., Abstr., 1907, i, 1045): (1) the *normal* salt, $C_{20}H_{24}O_2N_2,C_{21}H_{16}O_{11}$, and (2) the *basic* salt, $2C_{20}H_{24}O_2N_2,C_{21}H_{16}O_{11}$. The first of these salts is of therapeutical interest, as it contains a greater proportion of salicylic acid than any of the ordinary pharmaceutical preparations containing both salicylic acid and quinine. T. H. P.

Solubilities of True and False Tannates of Quinine. F. MURARO (*Gazzetta*, 1908, **38**, i, 427—430; *Boll. chim. farm.*, 1908, **47**, 255—258).—The author has determined the solubilities in water and dilute hydrochloric acid at 37° of the two true tannates of quinine having the composition (1) $C_{20}H_{24}O_2N_2,C_{14}H_{10}O_9,4H_2O$ and (2) $2C_{20}H_{24}O_2N_2,3C_{14}H_{10}O_9,8H_2O$, and of the false tannate (3) $2(C_{20}H_{24}O_2N_2,H_2SO_4),5C_{14}H_{10}O_9,14H_2O$. These solubilities are as follows: In water, (1) 0%, (2) 0%, (3) 0·313%. In 0·1% hydrochloric acid, (1) 0·984%, (2) 1·210%, (3) 0·847%, corresponding respectively with 0·443%, 0·448%, and 0·195% of quinine. In 0·3% hydrochloric acid, (1) 3·656%, (2) 4·756%, and (3) 1·560%, corresponding respectively with 1·645%, 1·760%, and 0·359% of quinine.

The two true tannates tend to liberate free tannic acid, and thus form more highly basic tannates, whilst the opposite is the case with the false tannate (3). Thus, when the last is washed for a long time with water, its composition becomes nearly that required by the formula $2(C_{20}H_{24}O_2N_2,H_2SO_4),7C_{14}H_{10}O_9,22H_2O$. T. H. P.

Ephedrine and ψ-Ephedrine. Ernst Schmidt (*Arch. Pharm.*, 1908, **246**, 210—214. Compare Abstr., 1904, i, 769; 1906, i, 602).—It has been suggested previously (*loc. cit.*) that when ephedrine is heated with hydrochloric acid an equilibrium mixture of ephedrine and ψ-ephedrine is formed. In the present paper, the validity of this view is established by the observation that each of these two substances can be converted into the equilibrium mixture, whence it appears certain that ephedrine and ψ-ephedrine are geometrical, not structural, isomerides. An attempt to form ψ-ephedrine from ephedrine by heating the latter at 213°, resulted in the partial decomposition of the base into methylamine and the isomeride of cinnamyl alcohol already obtained by Miller from ephedrine by a less direct method (Abstr., 1903, i, 110). A small amount of ψ-ephedrine is also formed in this reaction. T. A. H.

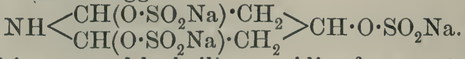
Preparation of Morphine Alkyl Bromides. J. D. Riedel (D.R.-P. 191088. Compare Abstr., 1906, i, 530).—The morphine alkyl bromides may be conveniently prepared by the interaction of the corresponding alkyl chlorides and hydrobromic acid or a soluble bromide. This double decomposition may be effected in aqueous alcoholic or acetone solutions. Morphine ethyl bromide and the corresponding methyl bromides were obtained in this manner.

G. T. M.

Pyridine. Hans Th. Bucherer and Julius Schenkel (*Ber.*, 1908, **41**, 1346—1352).—Körner's formula for pyridine represents this compound as containing the grouping $X\cdot N{:}CH\cdot X$, characteristic of Schiff's bases. According to Miller, the latter unite with sodium hydrogen sulphite. It is shown that pyridine also combines with sodium hydrogen sulphite, yielding a compound,

$$C_5H_5N,3NaHSO_3,2H_2O.$$

Substituted pyridines appear to react in a similar manner. The constitutional formula suggested is

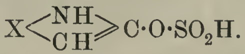


$$NH<\begin{matrix}CH(O\cdot SO_2Na)\cdot CH_2\\ CH(O\cdot SO_2Na)\cdot CH_2\end{matrix}>CH\cdot O\cdot SO_2Na.$$

The compound is prepared by boiling pyridine for twenty-four to thirty hours with a 40% sodium hydrogen sulphite solution, neutralising carefully with sodium carbonate, adding the requisite amount of barium iodide solution, filtering, evaporating the filtrate under reduced pressure, and precipitating with 96% alcohol. When rapidly heated, it decomposes at 235°, but when slowly heated it begins to decompose at 115°. It is readily decomposed by alkalis, yielding ammonia and a product with a characteristic odour. After warming for half an hour with alkali, the whole of the sulphur is present in the form of sulphite.

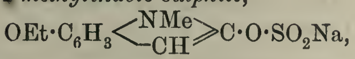
J. J. S.

Glycine and Indole Derivatives. Oscar Hinsberg (*Ber.*, 1908, **41**, 1367—1373).—The reaction between aromatic amines and glyoxal sodium hydrogen sulphite (Abstr., 1888, 372; 1892, 1458; 1895, i, 144; 1898, i, 275; Pschorr and Kuhtz, Abstr., 1905, i, 236; Pschorr and Karo, Abstr., 1906, i, 887) has been extended by the inclusion of the more complex amines: *p*-aminophenol, *p*-phenylenedimethyldiamine, 6-aminoquinoline, and methyl-*p*-phenetidine. Of these, only the last named yields an indolesulphonic acid; aminophenol and *p*-phenylenedimethyldiamine yield glycine derivatives, and aminoquinoline yields the compound $C_2H_2(O{\cdot}SO_2Na)_2(NH{\cdot}C_9H_6N)_2$.

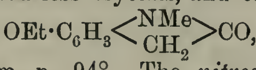
The formation of this compound indicates that in the reaction between an amine and the sodium bisulphite derivative of glyoxal, the first stage consists in the replacement of one or both of the hydroxyl groups by a substituted amino-group. If the resulting product is sparingly soluble, it can be isolated, but if readily soluble it loses sodium hydrogen sulphite, and by a process of molecular rearrangement yields a glycine derivative, or ring formation occurs and an indole derivative is formed. The compounds described previously as indolesulphonic acids are now regarded as esters derived from sulphurous acid and hydroxyindoles, for example,  $\mathrm{X}<\!\begin{matrix}\mathrm{NH}\\\mathrm{CH}\end{matrix}\!\geqslant\mathrm{C{\cdot}O{\cdot}SO_2H}$.

Phenylglycine is formed together with anilinoacetanilide by the action of aniline on glyoxal sodium bisulphite. *p*-Aminophenol and the bisulphite compound yield p-*hydroxyanilinoaceto*-p-*hydroxyanilide*, $OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}OH$, and *p*-hydroxyphenylglycine (Vater, Abstr., 1884, 1144). The former compound crystallises from dilute alcohol in colourless needles, m. p. 190°. The *hydrochloride* crystallises from water in colourless needles. *Tetramethyldiaminodiphenylglycineamide*, $NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2$, obtained from *p*-aminodimethylaniline and glyoxal sodium bisulphite, crystallises from dilute alcohol in glistening plates, m. p. 173°. It yields a soluble hydrochloride and a reddish-yellow nitrosoamine.

Sodium 5-ethoxy-1-methylindole sulphite,

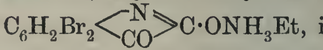


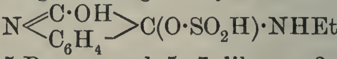
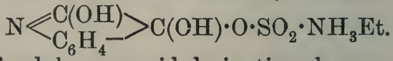
$$\mathrm{OEt{\cdot}C_6H_3}<\!\begin{matrix}\mathrm{NMe}\\\mathrm{-CH}\end{matrix}\!\geqslant\mathrm{C{\cdot}O{\cdot}SO_2Na},$$

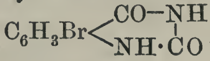
forms colourless crystals, and on hydrolysis yields 5-*ethoxy*-1-*methyloxindole*,  $\mathrm{OEt{\cdot}C_6H_3}<\!\begin{matrix}\mathrm{NMe}\\\mathrm{CH_2}\end{matrix}\!>\mathrm{CO}$, which crystallises from water in stout prisms, m. p. 94°. The *nitrosoamine*, $C_{11}H_{13}O_2N$, has m. p. 254° (decomp.).

Aminoquinoline glyoxaline bisulphite, $C_{20}H_{18}O_6N_4S_2$, forms an intensely yellow, crystalline powder with acidic properties, and is readily hydrolysed to sulphurous acid, glyoxal, and aminoquinoline.

J. J. S.

Action of Ethylamine on Isatin. C. HASLINGER (*Ber.*, 1908, 41, 1444—1453. Compare Abstr., 1907, i, 975).—The author has prepared other derivatives of the compounds obtained by the action of ethylamine on isatin. In addition to the three classes of compounds described previously, a fourth has been obtained by treating 5 : 7-dibromoisatin in chloroform and alcohol with 33% aqueous ethylamine, whereby 5 : 7-*dibromoisatin ethylamine*,  $C_6H_2Br_2<\genfrac{}{}{0pt}{}{N}{CO}>C{\cdot}ONH_3Et$, is precipitated, which separates from chloroform in violet-brown needles, readily changes to 5 : 7-dibromo-3-ethyliminoisatin by loss of water, and loses ethylamine by keeping or by treatment with dilute acids or alkalis.

By passing sulphur dioxide into an alcoholic suspension of 3-ethyliminoisatin, a white, crystalline substance is obtained, $C_{10}N_{12}O_4N_2S$, which readily loses sulphurous acid, regenerating 3-ethyliminoisatin, to which is ascribed the constitution  $N<\genfrac{}{}{0pt}{}{C{\cdot}OH}{C_6H_4}>C(O{\cdot}SO_2H){\cdot}NHEt$, or of the corresponding internal salt. 5-Bromo- and 5 : 7-dibromo-3-ethyliminoisatins yield analogous compounds. In addition to the preceding, compounds have been obtained containing one molecule of water more; they yield isatin under the influence of acids or alkalis, and consequently have constitutions such as  $N<\genfrac{}{}{0pt}{}{C(OH)}{C_6H_4}>C(OH){\cdot}O{\cdot}SO_2{\cdot}NH_3Et$. Members of both of these classes of sulphurous acid derivatives become brown and then violet on heating, resembling 3-ethyliminoisatin in this respect.

By prolonged treatment with alcoholic potassium hydroxide, the red crystals of the potassium salt of 3-ethyliminoisatin are changed to colourless crystals of a potassium salt, from which hydrochloric acid liberates a substance, $C_8H_8O_2N_2$, m. p. 343°, which is identical with benzoylenecarbamide (2 : 4-dioxy-1 : 3-quinazoline) (compare Abt, Abstr., 1889, 609; Gabriel and Colman, Abstr., 1905, i, 944). By distillation with lime, it yields *o*-aminobenzonitrile. In a similar manner, 5-bromo-3-ethyliminoisatin is converted into 6-*bromo*-2 : 4-*dioxy*-1 : 3-*quinazoline*,  $C_6H_3Br<\genfrac{}{}{0pt}{}{CO-NH}{NH{\cdot}CO}$, m. p. 354°.

C. S.

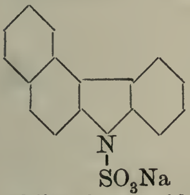
[A Double Salt from 8-Hydroxy-7-iodoquinoline-5-sulphonic Acid.] RICHARD GRIESE (D.R.-P. 190956).—The double *ammonium* salt, $C_9NH_4I(OH){\cdot}SO_3{\cdot}NH_4,NH_4I$, obtained in orange-yellow leaflets by concentrating an aqueous solution containing molecular proportions of ammonium 7-iodo-8-hydroxyquinoline-5-sulphonate and ammonium iodide, is very soluble in water or alcohol and decomposes at 225°. This compound has the germicidal properties of its components; dilute hydrochloric acid decomposes it, liberating iodine. These properties render it valuable in therapeutics.

G. T. M.

Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. V. Hans Th. Bucherer and Franz Seyde (*J. pr. Chem.*, 1908, [ii], 77, 403—413. Compare Abstr., 1903, i, 627; 1904, i, 309, 395; 1905, i, 48, 585; 1907, i, 509).—In analogy to the formation of aryl-substituted β-naphthylamines by the sulphite method, the immediate product of the action of phenylhydrazine on β-hydroxynaphthoic acid is *s*-phenyl-β-naphthylhydrazine,

$$C_{10}H_7\cdot NH\cdot NHPh.$$

The reaction, however, does not stop here; the product undergoes a further series of changes, leading to the formation of a sodium sulphaminate of 1 : 2-phenonaphthacarbazole, which has the annexed constitution. It is considered that the *s*-hydrazine undergoes oxidation to the azo-compound, which combines with sodium hydrogen sulphite, forming the intermediate substance, $C_{10}H_7\cdot NH\cdot NPh\cdot SO_3Na$, the last stage in the reaction being an intramolecular condensation of this, resembling Fischer's indole synthesis. A small amount of the sodium sulphaminate undergoes intramolecular change into a sodium sulphonate, whilst by a side-reaction small quantities of the *s*-hydrazine form 2-amino-1-*o*-aminophenylnaphthalene by the benzidine change. When heated above its m. p., the dihydrochloride of the diamino-compound decomposes, forming hydrogen chloride, ammonium chloride, and 1 : 2-phenonaphthacarbazole, thus confirming the ortho-position of the two amino-groups. The same products are obtained, but in smaller yields, from phenylhydrazine and β-naphthol. The interaction of *p*-tolylhydrazine and β-hydroxynaphthoic acid takes place in the same manner.



Sodium 1 : 2-*phenonaphthacarbazole*-N-*sulphonate*, $C_{16}H_{10}O_3NSNa$, is obtained in a 70% yield from β-hydroxynaphthoic acid, but only a 45% yield from β-naphthol; it crystallises from alcohol in white needles, is soluble in water, and when heated with mineral acid yields 1 : 2-phenonaphthacarbazole, m. p. 135° (Japp and Maitland, Proc., 1901, 186). The *barium* salt, $(C_{16}H_{10}O_3NS)_2Ba$, is crystalline.

On recrystallisation of the preceding sodium salt from alcohol, a small amount of an insoluble salt is obtained, which on acidification yields a *sulphonic acid*, $C_{16}H_{11}O_3NS$, crystallising in needles; it forms an aqueous solution with blue fluorescence, and couples with *p*-nitrodiazobenzene chloride, forming a weak violet *dye*.

2-*Amino*-1-o-*aminophenylnaphthalene*, $C_{16}H_{14}N_2$, crystallises from alcohol in glistening prisms, m. p. 154°, decomp. 160—200°, forming 1 : 2-phenonaphthacarbazole, is insoluble in water, forms a blue fluorescent solution in alcohol, and when diazotised and coupled with R-salt in alkaline solution forms a red *dye*, which dyes wool red, or unmordanted cotton a weak red.

On prolonged heating with dilute sodium hydrogen sulphite on the water-bath, hydrazobenzene is converted into benzidine.

Sodium 2′-*methyl*-1 : 2-*phenonaphthacarbazole*-N-*sulphonate*,

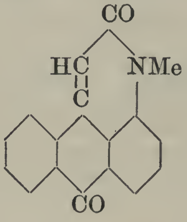
$$C_{17}H_{12}O_3NSNa,$$

prepared from *p*-tolylhydrazine and β-hydroxynaphthoic acid, crystallises in needles, and when heated with hydrochloric acid yields 2′-methyl-

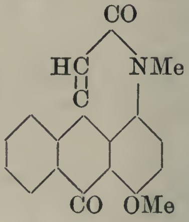
1 : 2-phenonaphthacarbazole, m. p. 181° (Ullmann, Abstr., 1904, i, 776). G. Y.

Preparation of Anthraquinone Derivatives Containing Nitrogen. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 192201).—The acyl derivatives of the secondary aminoanthraquinones undergo condensation, forming cyclic compounds containing a new nitrogen ring.

1-Acetylmethylaminoanthraquinone, when heated with aqueous sodium hydroxide, furnishes a condensation product (I) crystallising from pyridine in yellow needles :



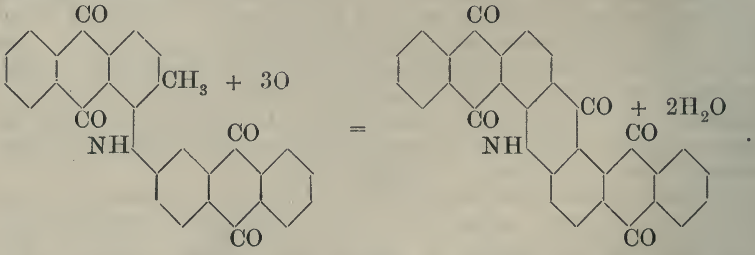
(I.)



(II.)

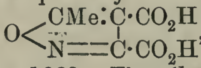
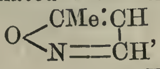
4-Nitro-1-acetylmethylaminoanthraquinone, when boiled for three hours with sodium and methyl alcohol, furnishes the compound (II). The patent contains references to thirteen other condensation products of this type, derived from derivatives of methylaminoanthraquinone. G. T. M.

[Oxidation of 2-Methyl-1 : 2′-dianthraquinonylamine.] Badische Anilin- & Soda-Fabrik (D.R.-P. 192436. Compare Abstr., 1907, i, 226).—A mixture of 2-methyl-1 : 2′-dianthraquinonylamine and litharge was added to fused potassium hydroxide at 170°, when an orange-red oxidation product was obtained in accordance with the following equation :



The compound crystallises from nitrobenzene, and in the hyposulphite vat it furnishes a violet colouring matter which dyes cotton in this shade, the dyed fabric slowly acquiring by oxidation of the violet vat dye a very fast, orange-red colour. G. T. M.

New Synthesis of *iso*Oxazoles. Julius Schmidt and Karl Th. Widmann (*Ber.*, 1908, 41, 1252—1260).—*iso*Oxazoles are formed by the action of red fuming nitric acid on γ-diketones. The reaction has been studied in the case of ethyl β-diacetylsuccinate, which, as

Knorr's investigations have shown, reacts both as a γ-diketone and a β-ketonic acid ester. By the action of red fuming nitric acid at a temperature of 0° to 5°, *ethyl 5-methyl*iso*oxazole-3 : 4-dicarboxylate* is formed, crystallising in large, colourless plates, m. p. 56—57°. On hydrolysis in the cold with the calculated quantity of normal alkali, *5-methyl*iso*oxazole-3 : 4-dicarboxylic acid*,  $\mathrm{O}<\begin{array}{l}\mathrm{CMe{:}C\cdot CO_2H}\\ \mathrm{N{=}{=}C\cdot CO_2H}\end{array}$, is formed, and crystallises in colourless needles, m. p. 183°. The *silver* salt is a colourless powder, which decomposes explosively when heated; the *copper* salt forms a green powder. When heated under special precautions at 185°, carbon dioxide is eliminated from the dicarboxylic acid, forming *5-methyl*iso*oxazole*,  $\mathrm{O}<\begin{array}{l}\mathrm{CMe{:}CH}\\ \mathrm{N{=}{=}CH}\end{array}$, b. p. 103—105°/20 mm. E. F. A.

Preparation of *p*-Nitrodiphenylamine and its Derivatives. Fritz Ullmann (D.R.-P. 193448).—4-Nitrodiphenylamine-2-sulphonic acid and its substitution products readily lose their sulphonic group on heating with mineral acid at temperatures not exceeding 100°.

4-Nitro-3′-amino-4′-methyldiphenylamine-2-sulphonic acid, when warmed with 5 parts of 80% sulphuric acid at 80—90° for ten to twenty minutes, dissolves completely, and *4-nitro-3′-amino-4′-methyldiphenylamine*, yellowish-red needles from toluene, m. p. 168°, is precipitated on the addition of alkali.

4-Nitrophenyl-4′-tolylamine, yellow needles from benzene, m. p. 139°, is similarly obtained from the sulphonic acid produced by condensing *p*-nitrochlorobenzene-*o*-sulphonic acid and *p*-toluidine.

3′-Chloro-4-nitrodiphenylamine, yellow leaflets, m. p. 129°, is prepared from 3-chloro-4-nitrodiphenylamine-2-sulphonic acid, and *4-nitro-4-hydroxydiphenylamine*, reddish-brown needles with steel-blue reflex, is obtained from the corresponding sulphonic acid. G. T. M.

Preparation of *p*-Aminodiphenylamine and its Derivatives. Fritz Ullmann (D.R.-P. 193351).—4-Aminodiphenylamine-2-sulphonic acid and its derivatives have now been found to undergo hydrolysis when heated with mineral acids at temperatures not exceeding 100°.

4-Amino-2-sulphodiphenylamine-2′-carboxylic acid, produced by heating anthranilic and *p*-chloronitrobenzene-*o*-sulphonic acids in aqueous sodium acetate and then reducing the nitro-compound obtained, is a colourless compound, forming soluble alkali salts and yielding *4-aminodiphenylamine-2-carboxylic acid* on heating at 100° with 60% sulphuric acid. The final product forms yellow needles, m. p. 200°, rapidly turning blue on exposure to air. G. T. M.

[2-Amino-4 : 6-diacetyldiaminophenol.] Leopold Cassella & Co. (D.R.-P. 191862).—*2-Amino-4 : 6-diacetyldiaminophenol* is prepared by reducing the nitro-compound obtained by treating 2 : 4′-diacetyldiaminophenol with excess of nitrous acid; it gives rise to a *diazo*-derivative, which readily couples to form azo-dyes with the sulphonic acids of the naphthols, aminonaphthols, dihydroxynaphthalenes, and naphthylenediamines. G. T. M.

Preparation of 6-Amino-2 : 4-diacetyldiaminophenol. LEOPOLD CASSELLA & Co. (D.R.-P. 191549).—6-*Nitro*-2 : 4-*diacetyldiaminophenol*, $NO_2 \cdot C_6H_2(NHAc)_2 \cdot OH$, yellow needles, m. p. 215°, is prepared by adding sodium nitrite solution to a thin paste of 2 : 4-diacetyldiaminophenol in dilute hydrochloric acid. On reduction with zinc dust and dilute sulphuric acid, this nitro-compound yields the *sulphate* of 2 : 4-*diacetyl*-2 : 4 : 6-*triaminophenol*; the free base forms colourless needles, m. p. 205°, which are readily soluble in water or alcohol and furnish a sparingly soluble diazo-derivative. G. T. M.

β-Phenylbenzylhydrazine. GIACOMO PONZIO and E. VALENTE (*Atti R. Accad. Sci. Torino*, 1908, **43**, 378—386 *).—Schlömann (Abstr., 1893, i, 452) described β-phenylbenzylhydrazine as a solid, m. p. 155°, but, on repeating his experiments, the authors were only able to obtain α-phenylbenzylhydrazine and benzaldehydephenylbenzylhydrazone, $CH_2Ph \cdot NPh \cdot N{:}CHPh$ (compare Minunni, Abstr., 1893, i, 97). Attempts to prepare β-phenylbenzylhydrazine by the interaction of benzyl bromide and phenylhydrazine (compare Fischer and Knoevenagel, Abstr., 1887, 932) in cold ethereal solution resulted in the formation of phenyldibenzylazonium bromide, $NH_2 \cdot NBrPh(CH_2Ph)_2$, and benzaldehydephenylbenzylhydrazone. When, however, phenylbenzylpiperazone is hydrolysed by means of 20% hydrochloric acid (compare Michaelis and Hermens, Abstr., 1892, 1494; 1893, i, 370), it yields succinic acid and β-phenylbenzylhydrazine hydrochloride. The authors' results show that the compound obtained by Paal and Bowedig (Abstr., 1892, 1455), and described as phenyldi-*o*-nitrodibenzylhydrazine, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, is really *o*-nitrobenzaldehyde-*o*-nitrophenylbenzylhydrazone,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NPh \cdot N{:}CH \cdot C_6H_4 \cdot NO_2.$$

Phenyldibenzylazonium bromide, $NH_2 \cdot NBrPh(CH_2Ph)_2$, crystallises from alcohol in shining, white prisms, m. p. 143°.

β-Phenylbenzylhydrazine, $CH_2Ph \cdot NH \cdot NHPh$, is obtained as a light, colourless oil, which oxidises rapidly in the air to benzylazobenzene, $CH_2Ph \cdot N{:}NPh$. Its *hydrochloride*, $C_{13}H_{14}N_2,HCl$, forms white laminæ, m. p. 193—195°. T. H. P.

Capacity of Acyl Groups for Migration in the Molecules of Organic Compounds. KARL AUWERS and H. DANNEHL (*Annalen*, 1908, **360**, 1—10. Compare Abstr., 1904, i, 736, 1051, 1053, 1054; 1907, i, 928).—This work was undertaken with the object of determining the capacity of acyl groups for intramolecular migration, and the conditions by which such migration is influenced. The present paper deals with the action of phenylhydrazine and its acyl derivatives on the acetate and benzoate of dibromo-*o*-hydroxybenzyl bromide, which leads to the formation of acyl-derivatives of the disubstituted *s*-hydrazine, $OH \cdot C_6H_2Br_2 \cdot CH_2 \cdot \underset{\alpha}{N}H \cdot \underset{\beta}{N}HPh$. In the nomenclature of the acyl derivatives, the two nitrogen atoms are distinguished as α-*N* and β-*N*, as indicated in the above formula.

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* and *Gazzetta*, 1908, **38**, i, 519—526.

It is found that the product of the action of phenylhydrazine on dibromo-*o*-acetoxybenzyl bromide, $OAc\cdot C_6H_2Br_2\cdot CH_2Br$, contains two *N*-acetyl compounds. One of these, the *β*-*N*-acetyl derivative,

$OH\cdot C_6H_2Br_2\cdot CH_2\cdot NH\cdot NPhAc$,

is formed also from dibromo-*o*-hydroxybenzyl bromide and *as*-acetylphenylhydrazine, $NH_2\cdot NPhAc$. Of the two constitutions,

$OH\cdot C_6H_2Br_2\cdot CH_2\cdot NAc\cdot NHPh$

and $OH\cdot C_6H_2Br_2\cdot CH_2\cdot NPh\cdot NHAc$, the former is ascribed to the second product, which is therefore the *α*-*N*-acetyl derivative, as the two isomerides when boiled with acetic anhydride yield the same triacetyl derivative, $OAc\cdot C_6H_2Br_2\cdot CH_2\cdot NAc\cdot NPhAc$, formed also by the action of acetic anhydride on the parent *s*-hydrazine and the *NN*-diacetyl derivative. This last substance,

$OH\cdot C_6H_2Br_2\cdot CH_2\cdot NAc\cdot NPhAc$,

is formed by the action of acetyl chloride on the *s*-hydrazine or its *β*-*N*-acetyl, but not the *α*-*N*-acetyl, derivative in cold pyridine solution, or by heating dibromo-*o*-acetoxybenzyl bromide with *as*- or *s*-acetylphenylhydrazide at 120—130°.

Somewhat different results are obtained with dibromo-*o*-benzoxybenzyl bromide. The action of phenylhydrazine on this leads to the formation of only one product, the *α*-*N*-benzoyl derivative,

$OH\cdot C_6H_2Br_2\cdot CH_2\cdot NBz\cdot NHPh$.

The isomeride, $OH\cdot C_6H_2Br_2\cdot CH_2\cdot NH\cdot NPhBz$, is prepared by the action of *as*-benzoylphenylhydrazide on dibromo-*o*-hydroxybenzyl bromide. Moreover, the product of the action of *as*-acetylphenylhydrazide on dibromo-*o*-benzoxybenzyl bromide is the *α*-*N*-acetyl-*o*-benzoyl derivative, $OBz\cdot C_6H_2Br_2\cdot CH_2\cdot NAc\cdot NHPh$. This substance is insoluble in alkalis, as is also the triacetyl derivative, whereas those compounds which contain a free hydroxyl are soluble.

It has been shown previously that an acetyl group attached to a phenolic oxygen atom may undergo transmigration to the first or second atom of a side-chain; the present results have extended this transmigration to the third atom. On what influences the differences observed in the behaviour of the acetyl and benzoyl groups depend remains for further investigation, as does also the question whether the transmigration of the benzoyl group is under all conditions limited to the second atom of the neighbouring side-chain.

s-*Phenyldibromo*-o-*hydroxybenzylhydrazine*, $C_{13}H_{12}ON_2Br_2$, prepared by heating 2 mols. of phenylhydrazine with 1 mol. of dibromo-*o*-hydroxybenzyl bromide in benzene solution, crystallises from alcohol in colourless needles, m. p. 163—164°. The *α*-N-*acetyl* derivative, $C_{15}H_{14}O_2N_2Br_2$, crystallises from alcohol in white plates, m. p. 183°, and is sparingly soluble in cold alcohol. The *β*-N-*acetyl* derivative forms white needles, m. p. 129—130°, and is readily soluble in alcohol. The two monoacetyl derivatives form mixed crystals, m. p. 134—136°. The *di*-N-*acetyl* derivative,

$C_{17}H_{16}O_3N_2Br_2$,

crystallises from alcohol in prismatic needles, m. p. 224°. The *triacetyl* derivative, $C_{19}H_{18}O_4N_2Br_2$, forms glistening needles, m. p. 143—145°.

If the product obtained by heating phenylhydrazine and dibromo-o-hydroxybenzyl bromide [sic] is treated with alkalis, there are obtained, in addition to the mixed crystals of the monoacetyl derivatives which form the chief product, small amounts of acetylphenylhydrazide, *s*-phenyldibromo-*o*-hydroxybenzylhydrazine, and a *substance*, $C_{22}H_{18}O_3N_2Br_4$, m. p. 240°, which must be formed by the introduction of an acetyl and two bromohydroxybenzyl groups into phenylhydrazine.

The α-N-*benzoyl* derivative, $C_{20}H_{16}O_2N_2Br_2$, crystallises in prismatic needles, m. p. 218—219°. The β-N-*benzoyl* derivative forms white prisms, m. p. 163—164°. The α-N-*acetyl*-o-*benzoyl* derivative,

$$C_{22}H_{18}O_3N_2Br_2,$$

crystallises from alcohol in white needles, m. p. 190—191°, and remains unchanged on prolonged boiling with acetic acid. G. Y.

Action of Nitrobenzene on Aldehydephenylhydrazones in the Light. Roberto Ciusa (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 369—374).—The reaction occurring between benzaldehydephenylhydrazone and nitrobenzene under the influence of light is quite similar to that between aldehydes and nitrobenzene (compare Ciamician and Silber, Abstr., 1906, i, 10), the hydrazone undergoing oxidation and the nitrobenzene reduction. Under these conditions, the oxidation products of benzaldehydephenylhydrazone are totally different from those obtained by the ordinary methods of oxidation; the main product is β-benzoylphenylhydrazine, and the change is represented by the scheme:

$$CHPh\colon N\cdot NHPh \longrightarrow OH\cdot CPh\colon N\cdot NHPh \rightleftarrows C_6H_5\cdot CO\cdot NH\cdot NHPh.$$

The reaction is complicated by the partial hydrolysis of the phenylhydrazone into aldehyde and phenylhydrazine, which react with the nitrobenzene and with its products of reduction. Other compounds isolated were benzaldehyde, benzoic acid, nitrosobenzene, benzylideneaniline, benzene, nitrogen, and a *base* giving a hydrochloride, m. p. 191°, which yields quinone when oxidised with chromic acid.

When heated together on a water-bath in the dark, benzaldehydephenylhydrazone and nitrobenzene react slowly, giving products different from those obtained under the action of light.

T. H. P.

Hydrazones of Aromatic Hydroxyketones. Alkali-insoluble Phenols. II. Henry A. Torrey and H. B. Kipper (*J. Amer. Chem. Soc.*, 1908, **30**, 836—861).—In an earlier paper (Abstr., 1907, i, 325) attention has been drawn to the insolubility of certain phenolic compounds in aqueous alkali hydroxides, and suggestions have been put forward in explanation of this behaviour. The work has been continued, particularly with reference to the phenylhydrazones and similar derivatives of resacetophenone and resodiacetophenone. These compounds are arranged in two groups, according to their solubility in alkali hydroxides. The following substances are soluble: Resacetophenone-phenylhydrazone, semicarbazone, and monoazine derivative; resodiacetophenone monophenylhydrazone, and bisazine derivative; and nitroresacetophenonephenylhydrazone. The following are insoluble: Phenylhydrazones of paeonol, 4-acetyl- and 4-benzoylresacetophenone, and 4-acetyl- and 4-benzoyl-resodiacetophenone; bisphenylhydrazones of resodiacetophenone and its 4-methyl ether, and of dibenzoylresorcinol, dibenzoylquinol, and bromoresodiacetophenone; bis-*p*-bromophenylhydrazone of resodiacetophenone, condensation product of benzidine and resodiacetophenone, and dianilinomonoazine derivative of resodiacetophenone. A discussion is given of the cause of the difference in solubility of these compounds, but no satisfactory explanation is at present available. In general, it may be said that the insolubility is due to the combined influence of a large group, such as $\cdot CH{:}N\cdot NHPh$ or $\cdot CMe{:}N\cdot NHPh$, in the ortho-position to the hydroxyl group and a carbon-containing group elsewhere in the ring, but whether it is due to an actual change in structure is not yet known. All the phenols which are insoluble in aqueous solutions of alkali hydroxide are readily soluble in alcoholic solutions, and can be reprecipitated by mineral acids.

The following compounds are described: *Resacetophenonephenylhydrazone 4-methyl ether*, $OMe\cdot C_6H_3(OH)\cdot CMe{:}N\cdot NHPh$, m. p. 108°; 4-*benzoylresacetophenonephenylhydrazone*,

$$OBz\cdot C_6H_3(OH)\cdot CMe{:}N\cdot NHPh,$$

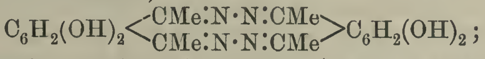
m. p. 181—182°; 4-*acetylresacetophenonephenylhydrazone*, m. p. 127—128°; *nitroresacetophenonephenylhydrazone*,

$$NO_2\cdot C_6H_2(OH)_2\cdot CMe{:}N\cdot NHPh,$$

m. p. 232—234° (decomp.); *resacetophenonesemicarbazone*, m. p. 214—220° (decomp.); *resodiacetophenonephenylhydrazone*,

$$COMe\cdot C_6H_2(OH)_2\cdot CMe{:}N\cdot NHPh,$$

m. p. 233° (decomp.); *bisphenylhydrazone* of *resodiacetophenone* 4-*methyl ether*, $NHPh\cdot N{:}CMe\cdot C_6H_2(OH)(OMe)\cdot CMe{:}N\cdot NHPh$, m. p. 245—246° (decomp.); 2:4-*diacetylresodiacetophenone*, m. p. 120°; 2:4-*dibenzoylresodiacetophenone*, m. p. 118—119°; 4-*acetylresodiacetophenonephenylhydrazone*, m. p. 214—215°; *resodiacetophenone bis*-p-*bromophenylhydrazone*, m. p. 270—271° (decomp.); *bromoresodiacetophenonebisphenylhydrazone*, which decomposes at 215—220°; *resodiacetophenonemonoazine*, $N_2[{:}CMe\cdot C_6H_2(OH)_2\cdot COMe]_2$, its *dianilino*-derivative, and the *bisazine*,



$$C_6H_2(OH)_2{<}\begin{matrix}CMe{:}N\cdot N{:}CMe\\ CMe{:}N\cdot N{:}CMe\end{matrix}{>}C_6H_2(OH)_2;$$

and a condensation *product* of benzidine (2 mols.) with resodiacetophenone (2 mols.).

The supposed dibenzoylresacetophenonephenylhydrazone, m. p. 183°, described previously (*loc. cit.*), is really the phenylhydrazone of the monobenzoyl derivative.

Experiments were carried out on the action of *m*-nitrobenzoyl chloride on diacetylquinol and diacetylresorcinol in presence of condensing agents, but in no case did the nitrobenzoyl group enter the ring, it merely replaced one or both of the acetyl groups.

E. G.

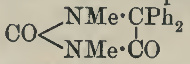
Action of α-Benzoylphenylhydrazine on Halogen Derivatives of Quinones. William McPherson and Wilbur L. Dubois (*J. Amer. Chem. Soc.*, 1908, **30**, 816—822).—It has been shown by

McPherson (Abstr., 1896, i, 127) that *a*-acylphenylhydrazines condense smoothly with benzoquinones and naphthaquinones to form hydrazones. The action of *a*-benzoyl-*a*-naphthylhydrazine on quinones has been studied by McPherson and Gore (Abstr., 1901, i, 572). A preliminary paper on the action of acylphenylhydrazines on the halogen derivatives of the quinones has already been published (McPherson and Fischer, Abstr., 1900, i, 411). This work has been continued, and it has been found that the reaction takes place in three different ways. (1) Condensation with the formation of hydrazones; the experiments which have been carried out indicate that this occurs only in the case of the monohalogen derivatives of the quinones. (2) One of the hydrogen atoms of the hydrazine molecule, together with one of the hydrogen atoms of the quinone, may be removed by the oxidising action of a second molecule of the quinone. Thus with trichloroquinone the following action takes place: $C_6HCl_3O_2 + C_6H_5{\cdot}NAc{\cdot}NH_2 + O = C_6Cl_3O_2{\cdot}NH{\cdot}NAcPh + H_2O$. (3) One of the hydrogen atoms of the hydrazine may combine with a chlorine atom of the quinone with elimination of hydrogen chloride; thus with tetrachloroquinone the reaction is as follows: $C_6Cl_4O_2 + NPhAc{\cdot}NH_2 = C_6Cl_3O_2{\cdot}NH{\cdot}NPhAc + HCl$.

Chlorobenzoquinonebenzoylphenylhydrazone, $C_6H_3ClO_2{:}N{\cdot}NBzPh$, m. p. 172·5°, forms yellow crystals, and on hydrolysis with sulphuric acid yields *benzeneazo*-o-*chlorophenol*, m. p. 86°, identical with the product of the action of diazobenzene chloride on *o*-chlorophenol.

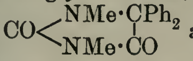
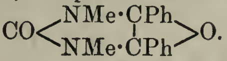
Benzeneazo-o-*chlorophenyl benzoate*, $OBz{\cdot}C_6H_3Cl{\cdot}N{:}NPh$, obtained by the action of benzoyl chloride on benzeneazo-*o*-chlorophenol, m. p. 109°, forms reddish-yellow needles, and is also produced when an ethereal solution of chloroquinonebenzoylphenylhydrazone is heated with anhydrous potassium hydroxide. When *o*-chlorobenzoquinone is warmed with a solution of *a*-benzoylphenylhydrazine sulphate in glacial acetic acid, *benzeneazo*-o-*chlorophenol sulphate*, m. p. 188—190° (decomp.), is produced, and forms dark red, silky needles. E. G.

Action of Diphenylhydroxyacetic Acid on Dimethylcarbamide. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 311—314).—The action of hydroxydiphenylacetic acid on *s*-dimethylcarbamide yields a compound identical with that obtained by Biltz (this vol., i, 218) by the interaction of benzil and *s*-dimethylcarbamide, and described by that author as 4 : 5-diphenyl-1 : 3-dimethylglyoxalone-4 : 5-oxide. This compound is hence a hydantoin derivative of the formula



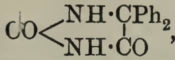
$CO\left<\begin{array}{l}NMe{\cdot}CPh_2\\ NMe{\cdot}CO\end{array}\right.$

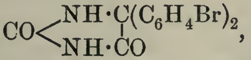
, and owes its formation to the glycol formed initially undergoing the pinacoline transformation, the group $-CPh(OH){\cdot}CPh(OH)-$ passing first into $-CPh_2{\cdot}C(OH)_2-$ and ultimately into $-CPh_2{\cdot}CO-$. T. H. P.

The Constitution of the Products obtained by the Action of Substituted Carbamides on Benzil, and New Methods for the Preparation of 5 : 5-Diphenylhydantoins. HEINRICH BILTZ and CHAIM RIMPEL (*Ber.*, 1908, 41, 1379—1393. Compare this vol., i, 218).—The products obtained by the condensation of benzil and *s*-dialkylcarbamides are now regarded as substituted hydantoins and not as glycol oxides, for example, the product from dimethylcarbamide as  $CO<\begin{matrix}NMe\cdot CPh_2\\ NMe\cdot CO\end{matrix}$ and not as  $CO<\begin{matrix}NMe\cdot CPh\\ NMe\cdot CPh\end{matrix}>O$. One reason for this change is that the same products are formed when benzilic acid is fused with dialkylcarbamides, and a second is the behaviour of the compounds towards alkalis. The condensation products from benzil and dialkylcarbamides are insoluble in alkalis, but condensation products in which there is the grouping CO·NH·CO are readily soluble; the alkali salts thus formed react with methyl or ethyl sulphate, yielding *N*-alkylated derivatives. The hydrolysis of 5:5-dialkylhydantoins to the corresponding hydantoic acid has not been accomplished.

A third argument in favour of the new formulæ is found in their behaviour towards oxidising agents. Glyoxalones react readily with chromic acid, yielding diacylated carbamides; both 4:5-diphenylglyoxalone and its glycol yield dibenzoyldimethylcarbamide, whereas the anhydride of the glycol yields no trace of this oxidation product and hence presumably contains a different grouping, namely, the hydantoin. The hydantoin constitution is also supported by the behaviour of the acetyl derivatives.

A simple method of obtaining these hydantoins is by boiling alcoholic solutions of benzil, substituted benzils, or other *α*-diketones with carbamide or monoalkyl carbamides in the presence of sodium or potassium hydroxide. Quantitative yields of pure product are obtained when the solution is diluted with water, filtered, and saturated with carbon dioxide. Dialkylated carbamides under similar conditions yield diphenyldialkylglyoxalone glycols, whereas benzilic acid and carbamides do not react.

5:5-*Diphenylhydantoin*,  $CO<\begin{matrix}NH\cdot CPh_2\\ NH\cdot CO\end{matrix}$, prepared by the action of alcoholic potassium hydroxide on the diphenylglyoxalone glycol, crystallises from alcohol and has m. p. 286°. It is not affected by concentrated nitric acid or chromic anhydride. It yields a *monoacetyl* derivative, $C_{17}H_{14}O_3N_2$, which crystallises from dilute alcohol in rectangular plates, m. p. 215—217°. 5:5-Diphenyl-3-methylhydantoin, obtained by the action of methyl sulphate on a solution of the diphenylhydantoin in sodium hydroxide, is identical with the product obtained by condensing benzil with methylcarbamide (this vol., i, 218). The corresponding *ethyl* derivative, $C_{17}H_{16}O_2N_2$, crystallises in compact, transparent rhombohedra, m. p. 155°.

5:5-*Di*-p-*bromophenylhydantoin*,  $CO<\begin{matrix}NH\cdot C(C_6H_4Br)_2\\ NH\cdot CO\end{matrix}$, is obtained as a by-product in the bromination of diphenylglyoxalone in acetic acid solution; it is also formed by the action of alcoholic potassium hydroxide on dibromodiphenylglyoxalone glycol or its ethers, or by condensing dibromobenzil and carbamide with alcoholic potash. It crystallises from alcohol in well-developed rhombohedra, m. p. 310° (corr.), and undergoes but slight decomposition when distilled under atmospheric pressure. It yields a *diacetyl* derivative, $C_{19}H_{14}O_4N_2Br_2$,

m. p. 187°, which is readily hydrolysed by water to the *monoacetyl* derivative, $C_{17}H_{12}O_3N_2Br_2$, m. p. 230°.

Dibenzoyldimethylcarbamide, $C_{17}H_{16}O_3N_2$, obtained by oxidising 4 : 5-diphenyl-1 : 3-dimethylglyoxalone or its glycol, crystallises from alcohol in plates, m. p. 162—163°.

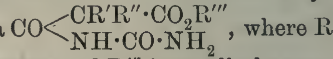
When 5 : 5-diphenyl-1 : 3-dimethylhydantoin is boiled with an acetic acid solution of chromic anhydride, the chief product is 1-*formyl*-5 : 5-*diphenyl-3-methylhydantoin*, $C_{17}H_{14}O_3N_2$, m. p. 162—163°, together with 5 : 5-diphenyl-3-methylhydantoin. J. J. S.

Preparation of 5 : 5-Dialkylbarbituric Acids. ALFRED EINHORN (D.R.-P. 193446).—The tetra-substituted diureides of the dialkyl malonic acids, $CX_2(CO\cdot NH\cdot CO\cdot NR_2)_2$, where R is an alkyl or acyl group, are converted into dialkylbarbituric acids by the action of acid condensing agents.

Diethylmalonyltetramethyldicarbamide,

$$CEt_2(CO\cdot NH\cdot CO\cdot NMe_2)_2,$$

white crystals, m. p. 158°, and *diethylmalonyltetraethyldicarbamide*, needles, m. p. 123—126°, are obtained by condensing diethylmalonyl chloride with *as*-dimethyl- and *as*-diethyl-carbamide respectively; the corresponding diphenyldimethyldiureide melts at 172°. These diureides, when heated with acids or zinc chloride, furnish 5 : 5-diethylbarbituric acid. G. T. M.

[Preparation of Barbituric Acid and its 5-Mono- and Di-alkyl Derivatives.] C. F. BOEHRINGER and SÖHNE (D.R.-P. 193447).—The diureides of the half acid esters of malonic and alkylmalonic acids, having the general formula  $CO<\begin{matrix}CR'R''\cdot CO_2R'''\\NH\cdot CO\cdot NH_2\end{matrix}$, where R′ and R″ are either hydrogen or an alkyl group, and R‴ is an alkyl group, have the property of condensing with alkaline agents to form barbituric acid and its 5-alkyl derivatives.

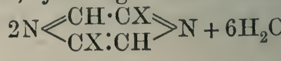
Ethyl malonylureide, $NH_2\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot CO_2Et$, prisms, m. p. 128°, obtained by the interaction of carbamide (2 mols.) and ethyl malonyl chloride, furnishes sodium barbiturate and alcohol on treatment with cold dilute aqueous sodium hydroxide.

Ethyl ethylmalonylureide, $NH_2\cdot CO\cdot NH\cdot CO\cdot CHEt\cdot CO_2Et$, m. p. 133°, gives rise to 5-ethylbarbituric acid (m. p. 191°).

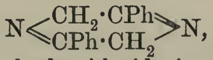
Ethyl diethylmalonylureide, $NH_2\cdot CO\cdot NH\cdot CO\cdot CEt_2\cdot CO_2Et$, m. p. 85°, and *methyl diethylmalonylureide*,

$$NH_2\cdot CO\cdot NH\cdot CO\cdot CEt_2\cdot CO_2Me,$$

m. p. 115°, both serve for the production of 5 : 5-diethylbarbituric acid, and the formation of this substance is induced either by ammonia or trisodium phosphate in aqueous solution. G. T. M.

Transformations of Amino-ketones. SIEGMUND GABRIEL [with ALBERT LIECK] (*Ber.*, 1908, **41**, 1127—1156. Compare this vol., i, 181, 274).—When α-aminoketones are liberated from their salts, they undergo oxidation and condensation, yielding disubstituted pyrazines, thus: $4X\cdot CO\cdot CH_2\cdot NH_2 + O_2 \longrightarrow$  $2N<\begin{matrix}CH\cdot CX\\CX{:}CH\end{matrix}>N + 6H_2O.$

This change has been thoroughly investigated, but whether the reaction takes place in two phases, namely, first condensation and then oxidation, or in one phase, namely, condensation of the two molecules as a result of oxidation, is still uncertain. Braun and V. Meyer (Abstr., 1888, 1093) have studied previously the action of alkalis on α-aminoacetophenone hydrochloride, but repetition of their work has shown that several of their statements are incorrect. The highly reactive secondary base, diphenacylamine, $NH(CH_2\cdot COPh)_2$, has been obtained by the action of ammonia on bromoacetophenone, and its chemical properties studied.

Diphenyldihydropyrazine,  $\mathrm{N}{<}\genfrac{}{}{0pt}{}{\mathrm{CH_2\cdot CPh}}{\mathrm{CPh\cdot CH_2}}{>}\mathrm{N}$, is formed when a solution of α-aminoacetophenone hydrochloride is neutralised with sodium hydroxide, sodium carbonate, or ammonia; it crystallises in orange-yellow, rhombic leaflets, m. p. 166—167°, and is converted, when boiled with hydrochloric acid, into α-aminoacetophenone. It undergoes oxidation when heated in the air at 100°, or when its alcoholic solution is boiled, yielding diphenylpyrazine, m. p. 194° (compare Harries and Gollnitz, Abstr., 1904, i, 427).

α-Aminoacetophenone hydrochloride yields, on treatment with an excess of alkali, a compound which is probably *anhydrobisphenacylamine*, $NH_2\cdot CH_2\cdot CPh{:}N\cdot CH_2\cdot COPh$; it crystallises in colourless, hexagonal leaflets, m. p. 130—133° (decomp.); the *nitrate*,

$$C_{16}H_{16}ON_2,2HNO_3,$$

crystallises in microscopic prisms, m. p. about 112—113° (decomp.); the *benzylidene* derivative, $C_{16}H_{14}ON_2{:}CHPh$, crystallises in small, colourless prisms, m. p. 163—164°. The parent substance loses water when it is heated alone or in acid solution, being converted into *bisanhydrophenacylamine* (*4-amino-3 : 5-diphenylpyrrole ?*), $C_{16}H_{14}N_2$, crystallising in flat, hexagonal plates or rhombohedra, m. p. 178—179°; the *platinichloride*, $(C_{16}H_{14}N_2)_2,H_2PtCl_6$, crystallises in flat, orange-red needles, which do not melt below 230°; the *hydriodide*, $C_{16}H_{14}N_2,HI$, crystallises in white, pointed needles, sintering above 200°, m. p. 220° (decomp.); the *nitrate* forms glistening needles, decomposing at 182—183°; the *hydrochloride* crystallises in long, flat, colourless needles; the *benzoyl* derivative, $C_{16}H_{13}N_2Bz$, crystallises in white prisms, m. p. 218—219°; the o-*hydroxybenzylidene* derivative,

$$C_{16}H_{12}N_2{:}CH\cdot C_6H_4\cdot OH,$$

crystallises in long, glistening, yellowish-green prisms, which sinter at 140°, m. p. 143° (decomp.); the *benzylidene* derivative, $C_{23}H_{18}N_2$, forms large, yellow, pointed prisms, which sinter at 140°, m. p. 144—145° (decomp.); it readily oxidises in the presence of benzaldehyde, yielding a *substance*, $(C_{23}H_{17}N_2)_2$, which crystallises in long, flat, reddish-brown needles with a dark brown, metallic reflex, m. p. 310°, and forming a bluish-violet liquid. Bisanhydrophenacylamine, when heated with hydriodic acid and red phosphorus, is converted into the *hydriodide* of a *base*, $C_{16}H_{15}ON,HI$; it melts and decomposes at 175°, forming an emerald-green liquid.

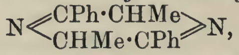
α-Bromoacetophenone is converted by aqueous ammonia into diphenyldihydropyrazine, diphenacylamine, and traces of diphenylpyrazine.

Diphenacylamine, $NH(CH_2{\cdot}COPh)_2$, obtained by treating its hydrochloride with sodium acetate, forms small, red crystals, which sinter at about 60°, m. p. 74—75°; the *hydrochloride*, $C_{16}H_{15}O_2N,HCl$, forms silvery leaflets, m. p. 235° (decomp.); the *platinichloride*, $(C_{16}H_{15}O_2N)_2,H_2PtCl_6$, crystallises in brown, rhombic leaflets or needles decomposing at 187—188°; the *aurichloride*,

$$C_{16}H_{15}O_2N,HAuCl_4,$$

crystallises in flat needles and scales, m. p. 168—169° (decomp.); the *picrate* forms long prisms, m. p. 170—171° (decomp.); the *nitroso*-derivative, $C_{16}H_{14}O_2N{\cdot}NO$, crystallises in glistening, yellow leaflets, m. p. 90°.

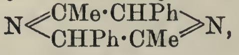
α-Aminopropiophenone hydrochloride, when treated with an equivalent amount of potassium hydroxide in aqueous solution, is converted into 3 : 6-*diphenyl*-2 : 5-*dimethyl*-2 : 5-*dihydropyrazine*,



$$\mathrm{N}{<}\begin{matrix}\mathrm{CPh{\cdot}CHMe}\\ \mathrm{CHMe{\cdot}CPh}\end{matrix}{>}\mathrm{N},$$

crystallising in short, lemon-yellow prisms, which sinter at 94°, m. p. 99—100°; the *hydrochloride*, $C_{18}H_{18}N_2,HCl$, forms brownish-red, hexagonal plates, m. p. 167—168°; the *oxalate*, $C_{18}H_{18}N_2,C_2H_2O_4$, crystallises in brownish-red needles, m. p. 182° (decomp.). The free base readily oxidises in the air, forming 3 : 6-diphenyl-2 : 5-dimethylpyrazine (compare Kolb, Abstr., 1896, i, 576); the compound, m. p. 125—126°, incorrectly described by Behr-Bregowski (Abstr., 1897, i, 458) as having the composition $C_{18}H_{18}ON_2$, is undoubtedly diphenyldimethylpyrazine. 3 : 6-Diphenyl-2 : 5-dimethyl-2 : 5-dihydropyrazine is converted by boiling hydrochloric acid partly into α-aminoacetophenone, but principally into α-amino-α-phenylacetone; the *platinichloride* of the latter, $(C_9H_{11}ON)_2,H_2PtCl_6$, forms brownish-yellow prisms, m. p. 192° (compare Kolb, *loc. cit.*).

α-Amino-α-phenylacetone hydrochloride is converted by aqueous ammonia into 3 : 6-*diphenyl*-2 : 5-*dimethyl*-3 : 6-*dihydropyrazine*,

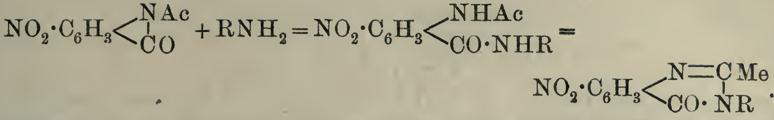


$$\mathrm{N}{<}\begin{matrix}\mathrm{CMe{\cdot}CHPh}\\ \mathrm{CHPh{\cdot}CMe}\end{matrix}{>}\mathrm{N},$$

crystallising in small, pale yellow needles, sintering at 95°, m. p. about 140° (in an evacuated capillary tube); the *hydrochloride*, $C_{18}H_{18}N_2,HCl$, crystallises in small, lemon-yellow, rhombic plates, m. p. 147°.

The free base rapidly oxidises in the air, forming 3 : 6-diphenyl-2 : 5-dimethylpyrazine. The compound described by Kolb (*loc. cit.*) as diphenyldimethyldihydropyrazine is probably slightly impure diphenyldimethylpyrazine. W. H. G.

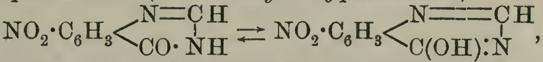
Quinazolones. XX. Certain 7-Nitro-2-methyl-4-quinazolones from 4-Nitroacetanthranil. MARSTON TAYLOR BOGERT and WILLIAM KLABER (*J. Amer. Chem. Soc.*, 1908, **30**, 807—816).—An account of the synthesis of 7-nitro-2-methyl-4-quinazolones has been given by Bogert and Steiner (Abstr., 1905, i, 945) and Bogert and Seil (Abstr., 1906, i, 712). The present investigation is an extension of this work. The reaction between 4-nitroacetanthranil and primary amines is expressed as follows:



$$NO_2\cdot C_6H_3{<}\begin{array}{l}NAc\\CO\end{array} + RNH_2 = NO_2\cdot C_6H_3{<}\begin{array}{l}NHAc\\CO\cdot NHR\end{array} = NO_2\cdot C_6H_3{<}\begin{array}{l}N{=}CMe\\CO\cdot NR\end{array}.$$

In some cases the intermediate amide was isolated. The primary amines employed were ammonia, methylamine, *n*-propylamine, benzylamine, β-naphthylamine, aniline, and *p*-anisidine. All these substances condensed smoothly and gave good yields.

7-*Nitro*-4-*quinazolone* (7-*nitro*-4-*hydroxyquinazoline*),

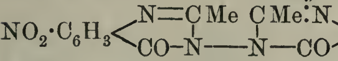


$$NO_2\cdot C_6H_3{<}\begin{array}{l}N{=}CH\\CO\cdot NH\end{array} \rightleftharpoons NO_2\cdot C_6H_3{<}\begin{array}{l}N{\equiv\!\equiv}CH\\C(OH){:}N\end{array},$$

m. p. 276° (corr.), obtained from 4-nitro-2-aminobenzoic acid and formamide, crystallises in long, slender, yellow needles.

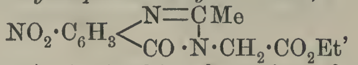
7-Nitro-2-methyl-4-quinazolone has m. p. 287—290° (corr.), and when oxidised with chromic acid yields a crystalline *substance*, m. p. about 327° (uncorr.). The *potassium* and *silver* salts of the quinazolone are described. 7-Nitro-2:3-dimethyl-4-quinazolone has m. p. 151—152° (corr.), and is nearly colourless. 7-*Nitro*-2-*methyl*-3-n-*propyl*-4-*quinazolone*, m. p. 140° (corr.), forms colourless needles. 7-*Nitro*-3-*phenyl*-2-*methyl*-4-*quinazolone*, m. p. 209° (corr.), crystallises in colourless, diamond-shaped plates. 7-*Nitro*-3-*benzyl*-2-*methyl*-4-*quinazolone*, m. p. 131—132° (corr.), forms yellow cubes; its *hydrochloride* has m. p. 229—230° (corr.). 7-*Nitro*-3-p-*anisyl*-2-*methyl*-4-*quinazolone*, m. p. 228° (corr.), crystallises in faintly yellow, lustrous scales. 7-*Nitro*-3-β-*naphthyl*-2-*methyl*-4-*quinazolone*, m. p. 218—219° (corr.), forms colourless needles.

7-*Amino*-2-*methyl*-4-*quinazolone* (7-*amino*-4-*hydroxy*-2-*methylquinazoline*), m. p. 311° (corr.), obtained by reducing the corresponding nitro-compound, forms long, silky, colourless needles. 7-*Nitro*-3-*amino*-2-*methyl*-4-*quinazolone*, m. p. 223° (corr.), prepared by the action of hydrazine hydrate on 4-nitroacetanthranil, crystallises in pale yellow needles. By the action of phenylhydrazine on this compound, a *substance*, m. p. 230° (uncorr.), is produced, and forms colourless, feathery needles. 7-*Nitro*-3-*acetylamino*-2-*methyl*-4-*quinazolone*, m. p. 233° (corr.), crystallises in short, colourless prisms; its *phenylhydrazone* has m. p. 315° (corr.). The corresponding *diacetyl* derivative, m. p. 132° (corr.), forms pale yellow plates.

7 : 7′-*Dinitro*-2 : 2′-*dimethyl*-4 : 4′-*diketotetrahydro*-3 : 3′-*diquinazolyl*,  $NO_2\cdot C_6H_3{<}\begin{array}{l}N{=}CMe\ \ CMe{:}N\\CO{-}N{-\!-\!-}N{-}CO\end{array}{>}C_6H_3\cdot NO_2$, m. p. 337·5° (corr.), obtained in small yield by heating 4-nitroacetanthranil with hydrazine hydrate, forms small, granular crystals; when treated with acetic anhydride, it yields a *compound*, m. p. 227° (uncorr.), which is probably an additive product.

When 4-nitroacetylanthranil (1 mol.) is heated with guanidine (1 mol.), *guanidine* 4-*nitroacetylanthranilate*, m. p. 247° (corr.), is produced; in one case, in which 2 mols. of the anthranil were used to 1 mol. of guanidine, a small quantity of a yellow *substance*, m. p. 253°, was obtained.

Ethyl 7-*nitro*-2-*methyl*-4-*quinazolonyl*-3-*acetate*,



$$NO_2\cdot C_6H_3{<}\begin{array}{l}N{=}CMe\\ CO\cdot N\cdot CH_2\cdot CO_2Et\end{array}$$

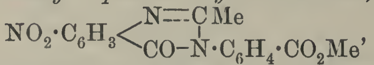
m. p. 139—140° (corr.), obtained by the action of ethyl aminoacetate on 4-nitroacetanthranil, forms colourless crystals. The corresponding *amide*, m. p. 275° (corr.), crystallises in silky needles, and the *nitrile*, m. p. 207—208° (corr.), in colourless, lustrous scales.

4-*Nitro*-2-*acetylaminohippuronitrile*,

$$NHAc\cdot C_6H_3(NO_2)\cdot CO\cdot NH\cdot CH_2\cdot CN,$$

m. p. 194° (decomp.), obtained as an intermediate product in the preparation of this quinazolone, forms colourless prisms, and is readily converted into the quinazolone by the action of hot dilute potassium hydroxide.

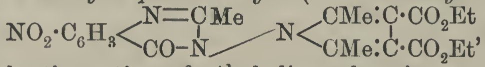
Methyl 7-*nitro*-2-*methyl*-4-*quinazolonyl*-3-o-*benzoate*,



$$NO_2\cdot C_6H_3{<}\begin{array}{l}N{=}CMe\\ CO{-}N\cdot C_6H_4\cdot CO_2Me\end{array}$$

m. p. 175° (corr.), obtained by heating 4-nitroacetylanthranil with methyl anthranilate, forms yellow, granular crystals. The *amide*, m. p. 320—321° (corr.), crystallises in straw-coloured needles. The *nitrile*, m. p. 234° (corr.), forms yellow needles.

7-*Nitro*-2-*methyl*-4-*quinazolonyl*-3-(2 : 5-*dimethyl*-3 : 4-*dicarbethoxypyrrole*),



$$NO_2\cdot C_6H_3{<}\begin{array}{l}N{=}CMe\\ CO{-}N\end{array}\!\!{-}N{<}\begin{array}{l}CMe{:}C\cdot CO_2Et\\ CMe{:}C\cdot CO_2Et\end{array}$$

m. p. 171° (corr.), obtained by the action of ethyl diacetylsuccinate on 7-nitro-3-amino-2-methylquinazolone, forms minute, colourless, lustrous scales. E. G.

Reaction of Indigotin with Potassium Permanganate. OSWALD MILLER and J. SMIRNOFF (*Ber.*, 1908, **41**, 1363—1367 [*]).—Pure indigotin has been obtained from natural and artificial indigo. The results of analysis agree well with the formula $C_{16}H_{10}O_2N_2$, and titrations with potassium permanganate in sulphuric acid solution indicate that 316·2 grams of permanganate oxidise 749·3 grams of indigotin, or 100 grams of indigotin require 42·26 grams of permanganate, numbers which confirm Mohr's results. The indigotin and permanganate solutions both contained 0·5 gram per litre, and preliminary experiments showed that concordant results are obtained when from 12·5 to 75 c.c. of indigotin solution are diluted with 600 c.c. of water purified by Hulett's method (Abstr., 1897, ii, 94), and the solution titrated with the permanganate. J. J. S.

Preparation of Tri- and Tetra-bromoindigotin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 193438).—The hitherto unknown *tribromoindigotin* may be obtained quantitatively by suspending indigotin in nitrobenzene or nitrotoluene, adding 2—2½ parts of bromine, and boiling the mixture at 225° for forty-five minutes, when the product separates as a violet-brown, crystalline powder. The employment of 3½ parts of bromine leads to the production of *tetrabromoindigotin* in voluminous, violet crystals. The tetrabromoindigotin prepared by leaving the indigotin, bromine, and nitrobenzene for twenty-four hours at the ordinary temperature and then heating at 130—135°, has slightly different tinctorial properties to

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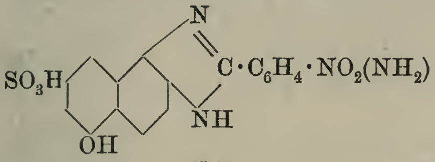
[*] and *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 625—637.

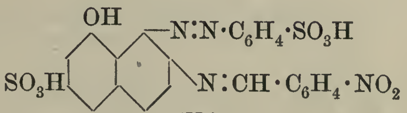
those of the substance produced at 225°. All these preparations are reduced in the hyposulphite vat, and give fast shades of blue on cotton.
G. T. M.

Preparation of Aminohydroxy-derivatives of Phenylnaphthiminazole. Actien Gesellschaft für Anilin- Fabrikation (D.R.-P. 193350).—5 : 6-Diamino-α-naphthol-3-sulphonic acid condenses with benzaldehyde and its derivatives to form benzylidene compounds, which are readily converted into phenylnaphthiminazole derivatives merely on warming with acids.

6-*Hydroxy*-2-m-*nitrophenyl-α-naphthiminazole*-8-*sulphonic acid* (I) is thus obtained from 5 : 6-diamino-α-naphthol-3-sulphonic acid and *m*-nitrobenzaldehyde by condensing these in dilute alcoholic solution and then warming the intermediate product with hydrochloric acid.



(I.)

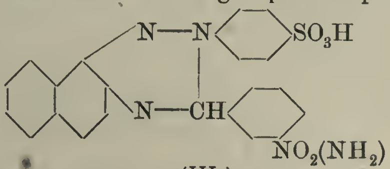

OH
$N{:}N\cdot C_6H_4\cdot SO_3H$
SO_3H
$N{:}CH\cdot C_6H_4\cdot NO_2$

(II.)

6-*Hydroxy*-2-m-*aminophenyl-α-naphthiminazole*-8-*sulphonic acid* results when the foregoing nitro-compound is reduced with iron and acetic acid.

Another naphthiminazole derivative results when the azo-derivative of 7-amino-α-naphthol-3-sulphonic acid and diazobenzenesulphonic acid is condensed with *p*-nitrobenzaldehyde and the resulting condensation product (II) reduced with stannous chloride, when the sulphanilic acid is regenerated and 9-*hydroxy*-2-p-*aminophenyl-α-naphthiminazole*-7-*sulphonic acid* is produced.

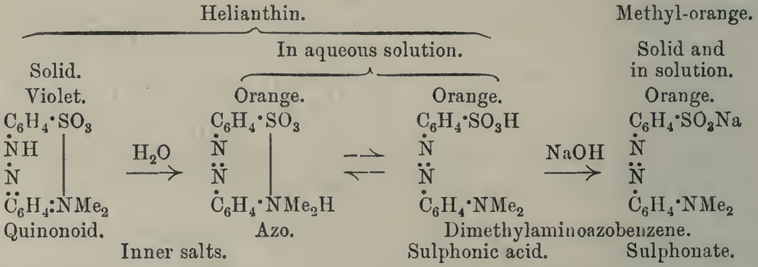
Although the benzylidene derivative gives rise to a naphthiminazole, yet the isomeric triazine (III) from *p*-sulphobenzene-8-azo-7-amino-α-naphthol-3-sulphonic acid can be reduced without fission of the triazine ring to give rise to an aminotriazinesulphonic acid which has the sweet taste characteristic of this group of compounds.



(III.)

G. T. M.

Establishment of the Isomerism Theory of Indicators in the Case of Methyl-orange and Helianthin. Arthur Hantzsch [and, in part, Friedrich Hilscher] (*Ber.*, 1908, 41, 1187—1195. Compare Hewitt, this vol., ii, 269).—As in the case of the salts of aminoazo-compounds (this vol., i, 484), the so-called free aminoazobenzenesulphonic acids, which in the solid state are undoubtedly inner salts, exist in two sharply-divided orange and violet forms. Thus, the so-called aminoazobenzenesulphonic acid and dimethylaminoazobenzenecarboxylic acid are orange, whilst the monomethyl-, dimethyl- and diethyl-aminoazobenzenesulphonic acids are violet. However, all alkali salts of these orange and violet acids are orange; they all show the same absorption spectrum, which is very similar to that of the free aminoazobenzenesulphonic acid and *p*-bromobenzeneazodimethylaniline, that is, they all have a similar azo-structure. Helianthin in the solid state is violet, and shows the characteristic selective band spectrum of the violet salts of aminoazo-compounds; it must therefore, like these, have a quinonoid structure. Its aqueous solution is, however, orange, and shows the same absorption spectrum as methyl-orange, from which it follows that helianthin, which in the solid state is an internal quinonoid salt, undergoes isomerisation during solution, changing into the azo-form. The relationship existing between these compounds may be shown thus:



Addition of an excess of a strong acid to the aqueous solution of helianthin turns it violet, and then shows the characteristic quinonoid absorption spectrum of the solid indicator and of the quinonoid violet amino-azo-salts. It is shown that the violet substance in the acidified solution of helianthin is not, for example, the quinonoid hydrochloride of helianthin, but the inner salt identical in structure with the solid indicator; the quinonoid hydrochloride can only be obtained, mixed with 10% of helianthin, by crystallising the latter from concentrated hydrochloric acid; further, to turn equivalent solutions of helianthin and benzeneazodibromoaniline violet, about 60 times as much acid is required in the latter case as in the former. It is therefore evident that the change of colour produced by adding acid to a dilute solution of methyl-orange or helianthin is due to the isomerisation of the orange dimethylaminoazobenzenesulphonic acid to the violet quinonoid internal salt:

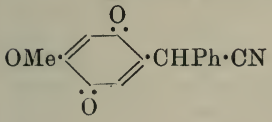
$$\mathrm{NMe_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_3H \longrightarrow \underbrace{NMe_2{\cdot}C_6H_4{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3}}$$

p-*Diethylaminoazobenzenesulphonic acid*, $NEt_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H$, is violet in the solid state; its *sodium*, *potassium*, and *ammonium* salts are orange. p-*Dimethylaminoazobenzenecarboxylic acid*,

$$NMe_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}CO_2H,$$

prepared by diazotising *p*-aminobenzoic acid and coupling with dimethylaniline, is orange; the *hydrochloride* is far more stable than the hydrochloride of helianthin; it crystallises in small, violet needles. The orange form of helianthin could not be isolated. W. H. G.

Preparation of Triazans. K. MICHAELIS (*Ber.*, 1908, 41, 1427—1433).—Through the great difference in the molecular magnitudes of the substituents in 5-methoxyquinone-2-benzyl cyanide, annexed formula, the author hoped to throw some light on the influence of steric hindrance in the formation of hydrazones, but the quinone and also others, such as benzoquinone, diethoxybenzoquinone, dibromodimethoxybenzoquinone, act usually as oxidising agents on substituted hydrazines. Methoxybenzoquinonebenzyl cyanide (1 mol.) and *as*-phenylbenzylhydrazine hydrochloride (2 mols.), heated in alcoholic solution, yield *diphenyldibenzyltriazan*,



$$C_7H_7\cdot NPh\cdot NH\cdot NPh\cdot C_7H_7,$$

m. p. 107°, which is also obtained by heating equal molecular quantities of *as*-phenylbenzylhydrazine and its hydrochloride at 180°, or by heating the hydrochloride alone. Minunni obtained the same compound in an impure state from carbamide and *as*-phenylbenzylhydrazine (Abstr., 1893, i, 97).

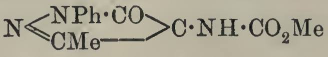
as-Diphenylhydrazine under the preceding conditions yields a violet dye, but equal molecular quantities of *as*-diphenylhydrazine and *as*-phenylbenzylhydrazine hydrochloride at 170—180° yield *triphenylbenzyltriazan*, $NPh_2\cdot NH\cdot NPh\cdot C_7H_7$, m. p. 120°, which, like diphenyldibenzyltriazan, is a stable substance, does not form salts, and gives a nitroso-derivative which responds to Liebermann's test.

Whilst *as*-phenylmethylhydrazine heated with an excess of carbamide at 170° yields Fischer's *as*-phenylmethylsemicarbazide, m. p. 135°, *as*-diphenylhydrazine and an equivalent quantity of carbamide at 180° give *tetraphenyldiaminobiuret*, $NPh_2\cdot NH\cdot CO\cdot NH\cdot CO\cdot NH\cdot NPh_2$, m. p. 253°, which also results quantitatively from biuret and *as*-diphenylhydrazine at 190°. The same compound is obtained by fusing *diphenylsemicarbazide*, $C_{13}H_{13}ON_3$, m. p. 195°, which is prepared readily by mixing aqueous solutions of equal molecular quantities of potassium cyanate and *as*-diphenylhydrazine hydrochloride.

as-*Phenylbenzylsemicarbazide*, $C_7H_7\cdot NPh\cdot N\cdot NH\cdot CO\cdot NH_2$, m. p. 103°, is prepared by adding an aqueous solution of potassium cyanate (1 mol.) to *as*-phenylbenzylhydrazine (1 mol.) dissolved in glacial acetic acid. By fusion with an equal molecular quantity of *as*-phenylbenzylhydrazine, it yields, not a triazan, but *diphenyldibenzyldiaminobiuret*, $C_7H_7\cdot NPh\cdot NH\cdot CO\cdot NH\cdot CO\cdot NH\cdot NPh\cdot C_7H_7$, m. p. 169°. C. S.

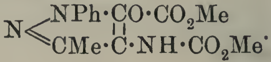
Preparation of 4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 189842).—4-Amino-1-phenyl-3-methyl-5-pyrazolone is readily oxidised to rubazonic acid by atmospheric oxygen, and on this account cannot be prepared conveniently on a technical scale. Its acyl and alkyl derivatives are more stable, and can be methylated to form 4-dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone (pyramidone).

1-*Phenyl*-3-*methyl*-4-*methylurethano*-5-*pyrazolone* (I), leaflets and needles, m. p. 198—199°, and 1-*phenyl*-3-*methyl*-4-*urethano*-5 *pyrazolone methyl carbonate* (II), slender needles, m. p. 153—154°, are obtained respectively by the action of one and two molecules of methyl chlorocarbonate on 4-amino-1-phenyl-3-methyl-5-pyrazolone:



$$\mathrm{N}{\lessdot}\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{CMe}\text{——}\end{matrix}{>}\mathrm{C\cdot NH\cdot CO_2Me}$$

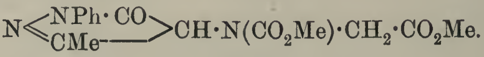
(I.)



$$\mathrm{N}{\lessdot}\begin{matrix}\mathrm{NPh\cdot CO\cdot CO_2Me}\\ \| \\ \mathrm{CMe\cdot C\cdot NH\cdot CO_2Me}\end{matrix}$$

(II.)

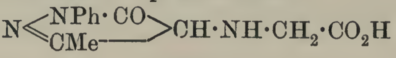
Either of the foregoing compounds when treated with methyl chloroacetate in presence of sodium methoxide gives rise to *methyl* 1-*phenyl*-3-*methyl*-4-*methylurethano*-5-*pyrazolonylacetate* (III), felted needles, m. p. 135—136°:



$$\mathrm{N}{\lessdot}\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{CMe}\text{——}\end{matrix}{>}\mathrm{CH\cdot N(CO_2Me)\cdot CH_2\cdot CO_2Me.}$$

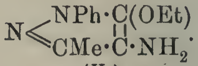
(III.)

When hydrolysed with dilute hydrochloric acid, the foregoing ester furnishes 4-*amino*-1-*phenyl*-3-*methyl*-5-*pyrazolonylacetic acid* (IV), leaflets from hot water, m. p. 193—194°:



$$\mathrm{N}{\lessdot}\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{CMe}\text{——}\end{matrix}{>}\mathrm{CH\cdot NH\cdot CH_2\cdot CO_2H}$$

(IV.)

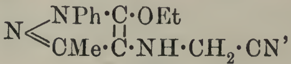


$$\mathrm{N}{\lessdot}\begin{matrix}\mathrm{NPh\cdot C(OEt)}\\ \| \\ \mathrm{CMe\cdot C\cdot NH_2}\end{matrix}$$

(V.)

4-*Amino*-5-*ethoxy*-1-*phenyl*-3-*methylpyrazole* (V), a non-crystallisable oil, obtained by reducing 4-benzeneazo-5-ethoxy-1-phenyl-3-methylpyrazole, forms a crystalline *hydrochloride*, m. p. 183—184°; *benzoyl* derivative, needles, m. p. 163—164°; *acetyl* derivative, needles, m. p. 99°.

4-*Cyanomethylamino*-5-*ethoxy*-1-*phenyl*-3-*methylpyrazole* (VI),

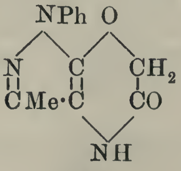


$$\mathrm{N}{\lessdot}\begin{matrix}\mathrm{NPh\cdot C\cdot OEt}\\ \| \\ \mathrm{CMe\cdot C\cdot NH\cdot CH_2\cdot CN'}\end{matrix}$$

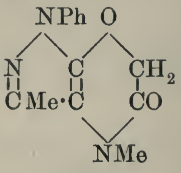
(VI.)

colourless crystals, m. p. 109—110°, is obtained by the action of formaldehyde and hydrocyanic acid on 4-amino-5-ethoxypyrazole.

The eso-*anhydride* of 4-*amino*-1-*phenyl*-3-*methylpyrazole*-5-*oxyacetic acid* (VII), thick crystals, m. p. 230°, is obtained by successively condensing the alkali derivative of 4-nitro-1-phenyl-3-methyl-5-pyrazolone with ethyl chloroacetate, and reducing the product:



(VII.)

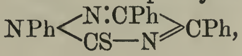


(VIII.)

This anhydride, although sparingly soluble in water, dissolves readily in concentrated hydrochloric acid or dilute aqueous sodium hydroxide. By treatment with methyl sulphate in alkaline solution, the *methyl* derivative (VIII) is formed, needles, m. p. 167—168°.

When the foregoing compounds are subjected to the action of methylating agents, the alkyl and acyl residues attached to a nitrogen or a pyrazolone oxygen atom are readily eliminated, and the valuable drug, 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone (pyramidone), is produced. G. T. M.

Aminophenylcarbamide and Aminophenylthiocarbamide. Luigi Rolla (*Gazzetta*, 1908, **38**, i, 327—349. Compare Pellizzari, Abstr., 1907, i, 873).—Like aminophenylcyanamide (compare Rolla, Abstr., 1907, i, 875), aminophenylcarbamide (α-phenylsemicarbazide) reacts readily with aldehydes and ketones and even with alloxan, yielding well-crystallised derivatives analogous to phenylhydrazones; this reaction is greatly accelerated by a trace of hydrochloric acid. Further, as a diamine, aminophenylcarbamide reacts with various compounds, such as benzil and glyoxal, yielding cyclic derivatives. With malonic acid, aminophenylcarbamide yields aminophenylbarbituric acid (?), a red, crystalline compound which is being studied further. With formic acid, aminophenylcarbamide yields 1-phenyl-1:2:4-triazole-5-one (compare Widman, Abstr., 1894, i, 57), whilst with carbamide it gives phenylurazole, already obtained by Pinner (Abstr., 1888, 687) by the action of carbamide on phenylsemicarbazide. Aminophenylthiocarbamide also reacts readily with aldehydes or ketones, giving phenylhydrazones. With benzil, too, it yields only a phenylhydrazone and not the thiontriphenyltriazine,



$$NPh<\begin{matrix}N:CPh\\CS—N\end{matrix}>CPh,$$

thus confirming the view that thiocarbamide reacts in accordance with its tautomeric formula, $NH_2\cdot C(SH):NH$.

Aminophenylcarbamide picrate, $NH_2\cdot NPh\cdot CO\cdot NH_2,C_6H_3O_7N_3$, has m. p. 163°.

m-*Nitrobenzylideneaminophenylcarbamide*,

$$NO_2\cdot C_6H_4\cdot CH:N\cdot NPh\cdot CO\cdot NH_2,$$

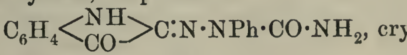
forms pale yellow crystals, m. p. 232°.

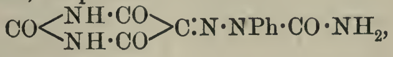
o-*Nitrobenzylideneaminophenylcarbamide*, $C_{14}H_{12}O_3N_4$, crystallises in pale yellow needles, m. p. 200°.

p-*Nitrobenzylideneaminophenylcarbamide*, $C_{14}H_{12}O_3N_4$, forms pale yellow, silky needles, m. p. 239°.

iso*Propylideneaminophenylcarbamide*, $CMe_2:N\cdot NPh\cdot CO\cdot NH_2$, separates from alcohol in white crystals, m. p. 137°.

Phenylethylideneaminophenylcarbamide, $CPhMe:N\cdot NPh\cdot CO\cdot NH_2$, is deposited from alcohol in white crystals, m. p. 122°.

Isatinaminophenylcarbamide,  $C_6H_4<\begin{matrix}NH\\CO\end{matrix}>C:N\cdot NPh\cdot CO\cdot NH_2$, crystallises from alcohol in yellow leaflets, m. p. 212°.

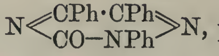
Alloxanaminophenylcarbamide,  $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C:N\cdot NPh\cdot CO\cdot NH_2$, separates in yellow flocks, m. p. 293°.

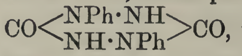
Ethyl acetoacetate-aminophenylcarbamide,

$$CO_2Et\cdot CH_2\cdot CMe:N\cdot NPh\cdot CO\cdot NH_2,$$

forms white crystals, m. p. 190°.

Aminophenylcarbamide forms a *copper* derivative, the *nitrate* of which, $Cu(C_7H_8ON_3)_2,2HNO_3$, separates from water in blue, acicular crystals, m. p. 155°.

Triphenyltriazine,  $\mathrm{N}<\begin{matrix}\mathrm{CPh\cdot CPh}\\ \mathrm{CO-NPh}\end{matrix}>\mathrm{N}$, prepared by the interaction of aminophenylthiocarbamide and benzil in alcoholic solution in presence of a trace of hydrochloric acid, separates from alcohol in pale yellow crystals, m. p. 170°, and gives a brilliant red coloration with concentrated sulphuric acid.

When heated at about 170°, aminophenylcarbamide condenses to the *diphenylurazine*,  $\mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot NH}\\ \mathrm{NH\cdot NPh}\end{matrix}>\mathrm{CO}$, which forms white crystals, m. p. 235° (compare Pinner, Abstr., 1888, 687).

Aminophenylthiocarbamide picrate, $C_7H_9NS_3,C_6H_3O_7N_3$, separates from water or alcohol in yellow crystals, m. p. 145°.

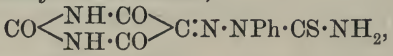
m-*Nitrobenzylideneaminophenylthiocarbamide*,

$$NO_2\cdot C_6H_4\cdot CH:N\cdot NPh\cdot CS\cdot NH_2,$$

separates from alcohol in yellow, acicular crystals, m. p. 211°.

iso*Propylideneaminophenylthiocarbamide*, $CMe_2:N\cdot NPh\cdot CS\cdot NH_2$, crystallises from alcohol in stellate aggregates of colourless needles, m. p. 135°.

Alloxanaminophenylthiocarbamide,



$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{C{:}N\cdot NPh\cdot CS\cdot NH_2},$$

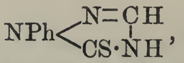
forms yellow crystals, m. p. 280°.

Ethyl acetoacetate-aminophenylthiocarbamide,

$$CO_2Et\cdot CH_2\cdot CMe:N\cdot NPh\cdot CS\cdot NH_2,$$

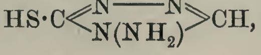
forms white crystals, m. p. 142°.

Benzilaminophenylthiocarbamide, $CPhBz:N\cdot NPh\cdot CS\cdot NH_2$, exists in two stereoisomeric forms, one red, m. p. about 100°, and the other white, m. p. 185°.

5-*Thion*-1-*phenyltriazolone*,  $\mathrm{NPh}<\begin{matrix}\mathrm{N=CH}\\ \mathrm{CS\cdot NH}\end{matrix}$, prepared by the action of formic acid on aminophenylthiocarbamide, crystallises from benzene in colourless, acicular laminæ, m. p. 178°, and is isomeric with the 3-thion-1-phenyltriazolone prepared by Pellizzari and Ferro (Abstr., 1899, i, 550) by the action of phosphorus pentasulphide on phenylurazole. T. H. P.

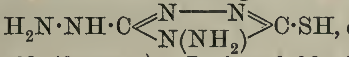
Thiocarbohydrazide. ROBERT STOLLÉ and P. E. BOWLES (*Ber.*, 1908, 41, 1099—1102).—A very convenient method of preparing thiocarbohydrazide is to heat a stirred aqueous solution of hydrazine dithiocarbazate (Curtius and Heidenreich, Abstr., 1894, i, 166) with lead oxide, when the filtrate deposits the compound in needles, m. p. 169°. *Dibenzylidenethiocarbohydrazide*, $CS(NH\cdot N:CHPh)_2$, forms pale yellow, glistening needles, m. p. 194°; the corresponding *ditolylidene* derivative, $C_{17}H_{18}N_4S$, crystallises from alcohol in yellow leaflets, m. p. 191°; the *bisnitrobenzylidenethiocarbohydrazide*, $C_{15}H_{12}O_4N_6S$, is pale yellow, m. p. 227°.

When heated with ethyl orthoformate in a sealed tube at 100°, thiocarbohydrazide forms 1-*amino*-2-*thiol*-1 : 3 : 4-*triazole*,

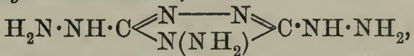


$$\mathrm{HS\cdot C}<\begin{matrix}\mathrm{N\!-\!\!-\!\!-N}\\ \mathrm{N(NH_2)}\end{matrix}>\mathrm{CH},$$

crystallising from alcohol in needles, m. p. 167°. Its aqueous solution is acid, giving a white precipitate with silver nitrate.

Hydrazine hydrate and thiocarbohydrazide when heated in a sealed tube for a long time at 120—130° give 1-*amino-5-thiol-2-hydrazino-1 : 3 : 4-triazole*,  $H_2N\cdot NH\cdot C{<}\begin{smallmatrix}N\text{——}N\\ N(NH_2)\end{smallmatrix}{>}C\cdot SH$, crystallising in slender needles, m. p. 228° (decomp.). It is soluble in alkali; its aqueous solution reduces ammoniacal silver nitrate in the cold; dilute nitric acid and silver nitrate give, however, a white precipitate.

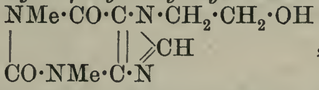
1-*Amino-*2 : 5-*dihydrazinotriazole*,

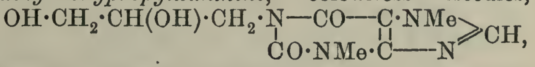


$$H_2N\cdot NH\cdot C{<}\begin{smallmatrix}N\text{——}N\\ N(NH_2)\end{smallmatrix}{>}C\cdot NH\cdot NH_2,$$

obtained by the action of hydrazine hydrate on guanidine carbonate, crystallises from dilute alcohol in slender, white needles, m. p. 207° (decomp.). Its aqueous solution reduces ammoniacal silver nitrate in the cold; the *hydrochloride* of its *tribenzylidene* derivative, $C_{23}H_{20}N_8,HCl$, separates in needles, m. p. 230°. W. R.

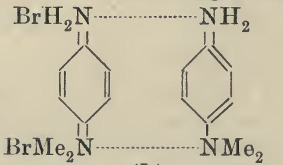
Preparation of Hydroxyalkyl Derivatives of Xanthine Bases. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 191106).—The therapeutic application of the xanthine bases is hindered by the poisonous secondary effect of these substances and their sparing solubility. Their hitherto unknown hydroxyalkyl derivatives, whilst retaining the powerful diuretic action of the parent bases, are free from the harmful secondary reaction and are readily soluble in water. These substances are prepared by the interaction of a xanthine base containing a replaceable hydrogen, and the halogen hydrins in the presence of some agent for fixing acid.

1 : 3-*Dimethyl-*7-*β-hydroxyethylxanthine*, colourless leaflets, m. p. 156—158°,  $\begin{array}{l}NMe\cdot CO\cdot C\cdot N\cdot CH_2\cdot CH_2\cdot OH\\ |\qquad\qquad \| \ {>}CH\\ CO\cdot NMe\cdot C\cdot N\end{array}$, is produced by heating together at 100—120° in aqueous solution theophylline, ethylene chlorohydrin, and sodium hydroxide; it does not form stable salts with acids or alkalis.

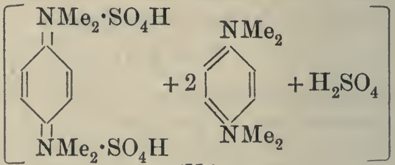
3 : 7-*Dimethyl-*1-*αβ-dihydroxypropylxanthine*, colourless needles, m. p. 153—155°,  $\begin{array}{l}OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot N\text{—}CO\text{—}C\cdot NMe\\ \qquad\qquad\qquad\qquad\quad |\qquad\qquad \|\qquad {>}CH,\\ \qquad\qquad\qquad\qquad\quad CO\cdot NMe\cdot C\text{——}N\end{array}$ is prepared from theobromine, ethylene monochlorohydrin, and aqueous sodium hydroxide.

3-*Methyl-*1 : 7-*ββ′-dihydroxydiethylxanthine*, from ethylene chlorohydrin and 3-methylxanthine, and *β-hydroxyethyltheobromine*, from this chlorohydrin and theobromine, form colourless needles melting respectively at 168—170° and 189—191°. G. T. M.

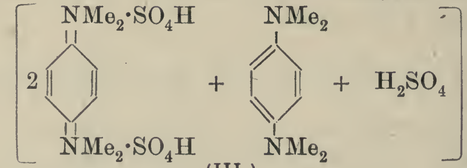
Quinonoid Compounds. XV. Wurster's Dye Salts. Richard Willstätter and Jean Piccard (*Ber.*, 1908, 41, 1458—1475. Compare Abstr., 1905, i, 669; 1906, i, 996; 1907, i, 641).—Wurster and Sendtner obtained an unstable, red dye by oxidation of *p*-aminodimethylaniline (Abstr., 1880, 110), whilst Wurster and Schobig obtained a similar, but blue, dye by oxidation of *p*-phenylenetetramethyldiamine (Abstr., 1880, 111). Bernthsen (Abstr., 1886, 53; 1889, 775) considered these dyes to be quinonoid compounds. The present authors have now obtained the two dyes as stable salts. Their constitution is discussed, and partially quinonoid formulæ ascribed to them. The red dye is a *meri* * quinonoid salt (I), whilst the blue dye is obtained in two states of oxidation, (II) and (III). In these formulæ, the parts of the molecules are considered to be united by the partial valencies of the nitrogen atoms:



(I.)



(II.)



(III.)

as-meri-Quinonedimethyldi-immonium bromide (I) is best prepared by the action of 1 atom of bromine on 1 mol. of *p*-phenylenedimethyldiamine in glacial acetic acid solution; it crystallises from methyl alcohol in black leaflets with metallic lustre, m. p. 146—147°, is green when powdered, remains unchanged on exposure to air, and forms bluish-red solutions, which are decolorised by addition of hydrochloric acid, or by reduction with stannous chloride or sulphurous acid, or by oxidation with ferric chloride or bromine. In the last case, the colourless solution becomes again red on addition of the leuco-chloride. In dilute hydrochloric acid solution, the dry salt turns potassium iodide-starch paper blue, and in concentrated aqueous solution forms a black, crystalline *iodide* on addition of potassium iodide. On addition of sodium thiosulphate, one-half of the aminodimethylaniline in the molecule is liberated.

as-*Quinonedimethyldi-immonium nitrate*,

$$NO_3{\cdot}NMe_2{:}C_6H_4{:}NH,HNO_3,$$

is obtained by the action of nitrous gases on *p*-phenylenedimethyldiamine; it forms colourless crystals, is unstable at the ordinary temperature, detonates when heated, yields Wurster and Sendtner's dye when boiled with alcohol, and forms a blue dye on addition of a salt of *p*-phenylenetetramethyldiamine.

The blue dye has been isolated as the *sulphate* (II); it crystallises in dark prisms with green metallic lustre, is dark violet when powdered, is stable in dry air, but smells of formaldehyde when exposed to moist air, and forms blue solutions. The action of nitrous gases on this dye leads to the formation of the two-thirds quinonoid *sulphate* (III), which is a weaker blue than the one-third quinonoid dye. G. Y.

* *μερικός*: partial.

Constitution of Hydroxyazo-compounds. KARL AUWERS (*Annalen*, 1908, 360, 11—25).—The evidence as to the constitution of those substances which have been held, on the one hand, to be hydroxyazo-compounds, and, on the other, to be quinonehydrazones, is summarised and discussed. The author considers that the weight of evidence is conclusively in favour of the hydroxyazo-structure for the ortho- as well as for the para-compounds.

Goldschmidt and Brubacher (Abstr., 1891, 1209) having failed to observe transmigration of the acyl group on reduction of *o*-nitrophenyl esters with zinc and acetic acid, considered that such transmigration could not take place on reduction in the same manner of acylated hydroxyazo-compounds. It is now found, however, that o-*nitro*-p-*tolyl benzoate*, $NO_2 \cdot C_6H_3Me \cdot OBz$, which is prepared by Schotten-Baumann's method from *o*-nitro-*p*-cresol, and crystallises from light petroleum in colourless needles, m. p. 102°, when reduced with zinc dust and acetic acid in the cold yields *o*-benzoylamino-*p*-cresol, $OH \cdot C_6H_3Me \cdot NHBz$. G. Y.

Measurement of the Effect of Certain Hypsochrome and Bathochrome Groups on the Colour of Azobenzene. HERBERT GORKE, ERNST KÖPPE, and FRITZ STAIGER (*Ber.*, 1908, 41, 1156—1171).—The work of Hantzsch and Glover (Abstr., 1907, i, 101) has been repeated and extended, using the same form of photometer, but employing as the source of light either a mercury lamp or a hydrogen tube instead of the unsatisfactory thallium flame.

The wave-lengths of the light employed were 576, 546, 486, 436, and 404 $\mu\mu$, and the substances examined were azobenzene, *p*-hydroxyazobenzene, and its methyl ether, ethyl ether, *propyl* ether, dark orange-red needles, m. p. 61°, *butyl* ether, orange-red leaflets, m. p. 67°, *phenyl* ether, golden-yellow leaflets, m. p. 116°, acetate, *propionate*, small, reddish-yellow needles, m. p. 75°, *butyrate*, orange leaflets, m. p. 77°, and benzoate. As in the case of the green of the thallium flame, Beer's law is also found to hold good in other parts of the spectrum.

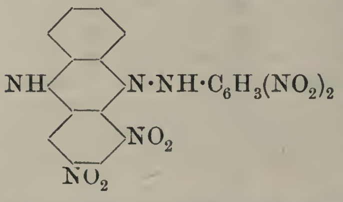
In the fused or solid state, none of the above substances exhibit any marked differences in colour intensity, but in each case examined, the effect of dissolving the substance, even in the most indifferent solvents, is to increase the molecular colour intensity, the effect being most marked in the case of the alkyl derivatives. The statement of Hantzsch and Glover (*loc. cit.*) that the intensities of the acyl and alkyl derivatives of *p*-hydroxyazobenzene in the same solvent are approximately proportional to the molecular weights does not hold good in other parts of the spectrum; in most cases, an increase in the mol. wt. is accompanied by a greater absorption in the green (546 $\mu\mu$) and bluish-green (486 $\mu\mu$) parts of the spectrum than in the blue and violet parts of the spectrum, whereas the introduction of an alkyl group into *p*-hydroxyazobenzene increases the absorption, the introduction of an acyl group decreases the absorption. As was shown by Hantzsch and Glover (*loc. cit.*), equivalent solutions of the same substance in various solvents exhibit varying colour intensities; this does not, however, appear to be directly related to any physical property of the solvent.

The effect of temperature on the colour intensity of a solution is very complicated; an increase in absorption in one part of the spectrum is accompanied by a decrease in another.

A marked increase in intensity accompanies the formation of a salt of *p*-hydroxyazobenzene; since the salt formation takes place without intramolecular rearrangement (compare Tuck, Trans., 1907, **91**, 450), Hantzsch's tenet, "a colourless substance which yields a coloured ion must be a ψ-acid," must be abandoned. W. H. G.

2:4:2′:4′:6′-Pentanitroazobenzene. H. Leemann and Eugène Grandmougin (*Ber.*, 1908, **41**, 1306—1309).—Pentanitrohydrazobenzene could not be obtained by the action of picrylhydrazine on chloro- or bromo-dinitrobenzene or from picryl chloride, chlorodinitrobenzene, and hydrazine hydrate, but when 2:4-dinitrophenylhydrazine (2 mols.) is heated with picryl chloride (1 mol.) at 110—120° for two hours the desired compound is obtained (compare Ciusa, Abstr., 1907, i, 875). Its *monopotassium* salt, $C_{12}H_6O_{10}N_7K$, is a dark explosive powder, dissolving in water with a red colour; the *dipotassium* salt is deep blue in solution and is easily hydrolysed.

2:4:6:2′:4′-*Pentanitroazobenzene*, $C_6H_2(NO_2)_3\cdot N\colon N\cdot C_6H_3(NO_2)_2$, obtained by the oxidation of the hydrazo-compound by lead peroxide, crystallises from glacial acetic acid in orange needles, m. p. 213°, and is not oxidised to the azoxy-compound by fuming nitric and chromic acids.



1:3-*Dinitro*-N-*dinitroanilinodihydrophenazine*, annexed formula, obtained by the action of pentanitroazobenzene on aniline at 100—115°, crystallises from a mixture of benzene and alcohol in lustrous, coppery-blue scales.

As the above substance has similar properties to Kehrmann and Messinger's dinitro-*N*-phenyldihydrophenazine (Abstr., 1894, i, 55), the above constitution is assigned to the substance. The parent substance dinitrodihydrophenazine could not be obtained by Kehrmann and Messinger's method, but is prepared by heating rapidly picryl-*o*-phenylenediamine in a naphthalene bath to 200°.

Picryl-o-phenylenediamine, $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_3$, obtained easily by action of picryl chloride on the diamine in alcoholic solution in the presence of potassium acetate at 50°, crystallises from xylene in small, cinnabar-red crystals, m. p. 177—178° (decomp.). W. R.

***s*-Hexanitroazobenzene.** H. Leemann and Eugène Grandmougin (*Ber.*, 1908, **41**, 1295—1305. Compare Abstr., 1907, i, 163).—The best method for preparing hexanitrohydrazobenzene is to add the hydrazine hydrate solution to a hot well-stirred alcoholic solution of picryl chloride, and then, as quickly as possible, potassium acetate (3 mols.), when the monopotassium salt separates. This salt,

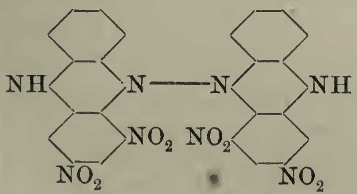
$C_{12}H_5O_{12}N_8K$, separates from its acetone solution on the addition of alcohol in metallic, green crystals, m. p. 188°, and the dipotassium salt, $C_{12}H_4O_{12}N_8K_2$, is also green; both salts are explosive, and the conclusion is drawn that they have a quinonoid structure (compare Hewitt and Mitchell, Trans., 1907, 91, 1254). The ammonium and potassium salts are sparingly, the sodium salts are easily, soluble. Hexanitroazobenzene (*loc. cit.*) appears to be dimorphous, and is extraordinarily stable towards acids, a mixture of fuming nitric and chromic acids having no action. It is, however, converted by dilute potassium hydroxide into hexanitrohydrazobenzene, picric acid, and decomposition products. Alcoholic hydrogen chloride, when heated with hexanitroazobenzene in a sealed tube at 130—150° for one and a half hours, forms 2 : 2′-*dichloro*-4 : 6 : 4′ : 6′-*tetranitroazobenzene*,

$$C_{12}H_4O_8N_6Cl_2,$$

which separates from a mixture of chlorobenzene and alcohol in orange needles, m. p. 244—245°. As ammonium sulphide reduces this compound to a hydrazo-derivative dissolving in alkali with a blue colour, the conclusion is drawn that the para positions are occupied by nitro-groups, and therefore that the compound has the above constitution (compare Werner and Stiasny, Abstr., 1900, i, 194).

Like other nitro-compounds, hexanitroazobenzene forms additive compounds with hydrocarbons, which contain 2 mols. of the hydrocarbon. The following have been prepared: that with *naphthalene* forms yellow, glistening needles, m. p. 165°; with *phenanthrene*, dark orange needles, m. p. 190°; with *anthracene*, brownish-red needles, m. p. 193°; an experiment to prepare one containing hexanitroazobenzene, anthracene, and naphthalene gave black needles, m. p. 208—210°, which proved to contain 2 mols. of the azo-compound with 1 mol. of anthracene. Also, α-nitronaphthalene, α- and β-ethoxynaphthalene, and α-naphthylamine yield additive compounds containing 2 mols. of the naphthalene derivative, which have m. p's. 124°, 158°, 137°, and 154° (decomp.) respectively.

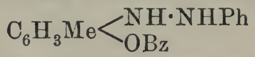
Primary amines, however, generally react with hexanitroazobenzene to form well-defined compounds. The reaction is a complicated one, and is dependent on the conditions of the experiment. Aniline gives aminoazobenzene, picrylaniline, *o*-trinitrobenzene, and *tetranitrohydrodiphenazine*, annexed formula, which crystallises from xylene in glistening, bluish-violet leaflets, m. p. 280°, decomp. 291°. It is best prepared by adding hexanitroazobenzene in small portions to a boiling solution of aniline in toluene. Molecular weight determinations by the boiling-point method in ethylene dibromide gave 569 and 588, calc. 542. When heated with alcoholic hydrochloric acid under pressure at 160°, it resulted in the replacement of the four nitro-groups by chlorine, *tetrachlorohydrodiphenazine*, $C_{24}H_{14}N_4Cl_4$, being formed. It crystallises in red needles, m. p. 350°.



o-Toluidine gives *tetranitrohydrodi*-o-*toluphenazine*, $C_{26}H_{18}O_8N_8$, crystallising in glistening, copper needles; *m*-toluidine, the corresponding *meta* compound, dark blue, almost black, needles, and *p*-toluidine, the *para* derivative, bluish-violet crystals. *Picryl*-m-*toluidine*, $C_{13}H_{10}O_6N_4$, forms golden-yellow leaflets, m. p. 126°. *Tetranitrohydrodi-β-naphthophenazine*, $C_{32}H_{18}O_8N_8$, crystallises from xylene in small, green needles. W. R.

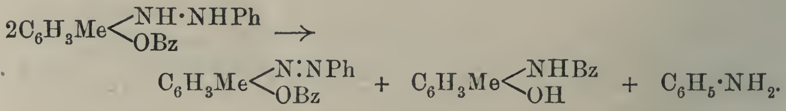
Azo-compounds from the *o*-Aminophenols and 2:8-Dihydroxynaphthalene-6-sulphonic Acid. Chemische Fabrik Griesheim-Elektron (D.R.-P. 191445).—When coupled with the diazotised aminophenols in sodium hydroxide or carbonate solutions, 2 : 8-dihydroxynaphthalene-6-sulphonic acid furnishes only poor yields of azo-derivatives, but in the presence of calcium hydroxide the condensation occurs extremely readily, and the products, when dyed on wool and subsequently chromed, furnish very fast shades of black. G. T. M.

Acyl Derivatives of Benzeneazo-*p*-cresol and *β*-Benzeneazo-*α*-naphthol and their Transformation Products. Karl Auwers and M. Eckardt (*Annalen*, 1908, **359**, 336—382).—With the object of throwing light upon the transformation of hydroxyazo-compounds, the investigation of the wandering of acid radicles (Abstr., 1904, i, 736) has been extended. Evidence in favour of the formula



$$C_6H_3Me\Big<\begin{array}{l}NH\cdot NHPh\\OBz\end{array}$$

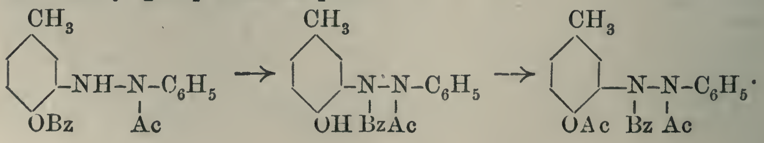
for the reduction product of benzeneazo-*p*-cresol benzoate is found (1) by heating the benzoylhydrazo-compound dissolved in glacial acetic acid, when simultaneous oxidation and reduction take place according to the scheme :

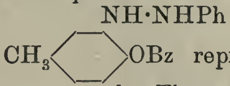


$$2C_6H_3Me\Big<\begin{array}{l}NH\cdot NHPh\\OBz\end{array} \longrightarrow C_6H_3Me\Big<\begin{array}{l}N{:}NPh\\OBz\end{array} + C_6H_3Me\Big<\begin{array}{l}NHBz\\OH\end{array} + C_6H_5\cdot NH_2.$$

(2) The benzoylhydrazo-compound in alcoholic solution undergoes the benzidine or semidine transformation with hydrogen chloride, the hydrochloride, m. p. 260°, separates out, and from this substance alkalis liberate a crystalline *anhydro-base*, m. p. 154—155°, the *sulphate* of which separates from water in silky needles, m. p. 250°. (3) Pyridine solutions of the benzoylhydrazo-compound give with excess of acetyl chloride the N-*β-monoacetyl* derivative, m. p. 143° ; hydroazobenzene behaves in a like manner.

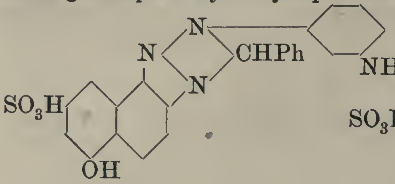
The *benzoyldiacetyl* derivative, m. p. 172·5°, when treated with alcoholic soda, becomes partly hydrolysed to a *monobenzoylacetyl* derivative, m. p. 151°, isomeric with that of m. p. 143°. Experiments show that when boiled with acetic anhydride the benzoyl group wanders from the oxygen to the neighbouring nitrogen atom and a second acetyl group takes its place :

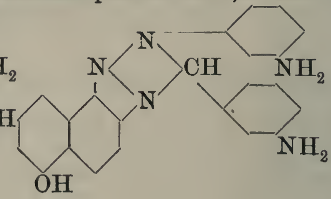


O-N_β-*Dibenzoylbenzenehydrazo*-p-*cresol*, m. p. 92°, has been prepared, and on reduction this gives *N*-benzoyl-*o*-amino-*p*-cresol and benzanilide. In like manner, the *benzoylanisoylhydrazo*-compound, m. p. 95—100°, gives *N*-benzoyl-*o*-amino-*p*-cresol and anisanilide. The conclusion is arrived at that  represents the reduction product of benzoylbenzeneazo-*p*-cresol. The authors find that at the temperature of the water-bath, the reduction of benzoylbenzeneazo-*p*-cresol proceeds further than Goldschmidt found at 0°, *o*-amino-*p*-cresol, its *N*-benzoyl derivative, aniline, and benzanilide having been isolated. The presence of benzanilide is evidence of the wandering in one part of the molecule of the acid radicle from the oxygen to the nitrogen atom. These and other considerations lead to the conclusion that benzeneazo-*p*-cresol benzoate, like its reduction product, is an *O*-ester. The constitution of the reduction product of acetylbenzeneazo-*p*-cresol (Abstr., 1891, 1209; 1907, i, 554) differs from that of the benzoyl derivative in that the acid radicle is united with nitrogen and not with oxygen; this is shown by the sole formation of acetanilide and free *o*-amino-*p*-cresol when treated with zinc and acetic acid. Only one benzoyl derivative of β-benzeneazo-α-naphthol could be obtained, and this on reduction gives aniline and the *N*-benzoate of β-amino-α-naphthol. Similarly, only one acetyl compound could be prepared, the mode of formation of which shows that a wandering has taken place in the molecule. On reduction by zinc and acetic acid, aniline and acetanilide are produced, showing that the compound is an *O*-ester, although it is also obtained from acetylphenylhydrazine and naphthaquinone, an isomeric change occurring in the latter case. J. V. E.

α-Anthramine and 1:4-Anthradiamine. Ilie J. Pisovschi (*Ber.*, 1908, 41, 1434—1436).—1-Anthramine is obtained in 70—80% yield by heating 1-anthrol with three or four times its weight of ammoniacal calcium chloride at 200—220° for one day, and has m. p. 119° (compare Dienel, Abstr., 1905, i, 767). 4-*Anthraceneazo*-1-*anthramine*, $C_{14}H_9{\cdot}N_2{\cdot}C_{14}H_8{\cdot}NH_2$, m. p. 239°, obtained from amyl nitrite (1 mol.) and 1-anthramine hydrochloride (2 mols.) in alcoholic solution, crystallises in reddish-brown needles with a green reflex, and forms unstable salts. *Benzeneazo*-1-*anthramine*, $Ph{\cdot}N_2{\cdot}C_{14}H_8{\cdot}NH_2$, m. p. 130°, prepared by mixing an aqueous solution of diazobenzene chloride with an alcoholic solution of 1-anthramine, forms red needles, and yields a deep blue *hydrochloride*, $C_{20}H_{15}N_3,HCl$, which is reduced by zinc dust and dilute hydrochloric acid to 1:4-*anthradiamine hydrochloride*; the corresponding *sulphate* crystallises in sparingly soluble, white needles. The *diacetyl* derivative, $C_{14}H_8(NHAc)_2$, has m. p. 322°. An acidified aqueous solution of 1:4-anthradiamine is oxidised by ferric chloride to yellow needles of 1:4-anthraquinone, which darkens at 210°, and has m. p. 218° (decomp.) (compare Dienel, Abstr., 1906, i, 290; Haslinger, *ibid.*, i, 967). C. S.

[Azo-derivatives of Naphthalenoid Triazines.] LEOPOLD CASSELLA & Co. (D.R.-P. 191024. Compare Abstr., 1907, i, 451).—The following complex hydroxynaphthatriazinesulphonic acids, I and II,


(I.)


(II.)

condense with diazonium salts in alkaline solutions, giving rise to azo-dyes, which have the valuable properties of dyeing unmordanted cotton and of undergoing diazotisation on the fibre with subsequent formation of fast ingrain colours with the ordinary developers (β-naphthol, &c.). These triazines are produced by the interaction of 6-amino-α-naphthol-3-sulphonic acid, a benzenoid amine, and benzaldehyde or its derivatives.

m-Nitroaniline and aniline have been employed as bases, and *m*-aminobenzaldehyde has been used instead of benzaldehyde.

G. T. M.

[Reactivity of Diazo-salts of 2 : 5-Dichloroaniline.] JOSEF ROHNER (D.R.-P. 193211).—2 : 5-Dichloroaniline furnishes a diazo-compound which greatly exceeds *p*-nitrodiazobenzene chloride in reactivity; it couples very readily with diethyl-*o*-toluidine and the para-substituted phenols, yielding azo-compounds having valuable tinctorial properties. The base is readily diazotised in 7% hydrochloric acid.

G. T. M.

Action of Diazo-salts on Phenyldinitromethane. [ω-Dinitrotoluene.] GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1908, **43**, 303—314; *Gazzetta*, 1908, **38**, i, 509—519).—The author describes the diazobenzene derivative of ω-dinitrotoluene and two isomeric compounds, one white and the other red, into which it is readily transformed.

The white compound is either α-nitro-β-nitroso-α-benzoyl-β-phenylhydrazine, $NO_2\cdot NBz\cdot NPh\cdot NO$, or $NO_2\cdot O\cdot CPh{:}N\cdot NPh\cdot NO$. The ready formation of this compound from the diazobenzene derivative of ω-dinitrotoluene indicates that the latter has the structure

$$NPh{:}N\cdot O\cdot CPh(NO)\cdot NO_2,$$

and is a change analogous to the transformation of an azo-compound into a hydrazone observed by Dimroth and Hartmann (Abstr., 1907, i, 1090). The potassium derivative of ω-dinitrotoluene, from which the diazobenzene derivative is obtained, is therefore regarded as having the structure $OK\cdot CPh(NO)\cdot NO_2$. The red isomeride is ω-benzeneazo-ω-dinitrotoluene, $NPh{:}N\cdot CPh(NO_2)_2$, which is the first known compound containing the groups NO_2 and $\cdot N{:}NAr$ united with one and the same carbon atom. Its formation from the diazobenzene derivative is explained by assuming that ω-dinitrotoluene can exist in two forms, one stable, $CHPh(NO_2)_2$, and the other labile, $NO_2\cdot CPh\colon NO\cdot OH$, which has not yet been isolated; if, then, the diazo-derivative has the structure $NO_2\cdot CPh\colon NO\cdot O\cdot N\colon NPh$, its spontaneous transformation into ω-benzeneazo-ω-dinitrotoluene represents a passage to the stable form.

The *diazobenzene* derivative of *ω-dinitrotoluene*, $C_{13}H_{10}O_4N_4$, forms golden-yellow crystals, m. p. 70°, and reacts with alcohol, yielding ω-dinitrotoluene, nitrogen, acetaldehyde, and benzene.

a-Nitro-β-nitroso-a-benzoyl-β-phenylhydrazine, $NO_2\cdot NBz\cdot NPh\cdot NO$, formed by the isomerisation of the diazobenzene derivative of ω-dinitrotoluene dissolved in benzene, chloroform, or carbon disulphide, forms shining, white laminæ, m. p. 127°, gives an emerald-green coloration with concentrated sulphuric acid and phenol, and reacts with cold water, yielding nitrosobenzoylphenylhydrazine (compare Voswinckel, Abstr., 1901, i, 617), and with boiling water, yielding benzoylphenylhydrazine, $NHBz\cdot NHPh$.

ω-Benzeneazo-ω-dinitrotoluene, $NPh\colon N\cdot CPh(NO_2)_2$, obtained when the isomeric diazobenzene compound is either left for eight to ten days or dissolved in the cold in alcohol, ether, or acetone, crystallises from chloroform in flattened, red needles, m. p. 138—147° (decomp.), and is far more stable than its two isomerides. T. H. P.

[Interaction of Diazo-salts and Aromatic Amides of the Higher Fatty Acids.] NATHANAEL SULZBERGER (D.R.-P. 193451. Compare this vol., i, 226).—*p*-Aminostearinanilide, prepared either by condensing together stearic acid and *p*-phenylenediamine or by nitrating stearinanilide and reducing the resulting *p*-nitrostearinanilide, yields a red azo(?)-colouring matter when treated with diazobenzene chloride.

Aminopalmitin-β-naphthalide is produced by condensing β-naphthylamine and palmitic acid at 250—300°, nitrating the palmitin-β-naphthalide thus produced, and reducing the mononitro-compound with zinc dust and hydrochloric acid; it couples with diazobenzene chloride and diazotised benzidine to yield respectively brownish-red and yellow colouring matters. G. T. M.

Reaction between Diazo-compounds and Azo-dyes. A. LWOFF (*Ber.*, 1908, 41, 1096—1097).—Griess (this Journ., 1876, ii, 416) has already shown that bisbenzeneazophenol is formed from *p*-hydroxybenzoic acid, carbon dioxide being eliminated. It is now shown that the group $SO_3H\cdot C_6H_4\cdot N_2\cdot$ is displaced from *p*-sulphobenzeneazo-β-naphthol by the action of *p*-nitro- and *o*-chloro-*p*-nitro-diazobenzene chlorides with the formation of the corresponding azo-β-naphthols. W. R.

Reaction between Diazo-compounds and Azo-dyes. EUGÈNE GRANDMOUGIN (*Ber.*, 1908, 41, 1403. Compare Lwoff, preceding abstract).—Examples of the removal of the azo-group from an azo-dye have been described previously (Abstr., 1907, i, 987; 1891, 1075). J. J. S.

Yellow Azo- and Violet Quinonoid Salts of Aminoazo-compounds. ARTHUR HANTZSCH and FRIEDRICH HILSCHER (*Ber.*, 1908, **41**, 1171—1187).—Although Thiele has shown (Abstr., 1904, i, 208) that *p*-aminoazobenzene hydrochloride can be obtained both in violet and flesh-red modifications, other cases have not hitherto been described. It is found that the salts of aminoazo-compounds exist in two isomeric forms, which are coloured either orange-yellow or bluish-violet. The colour of the salt is determined by the nature of the acid and of the aminoazo-compound; *p*-dimethylaminoazobenzene, *p*-anilinoazobenzene, *p*-dimethylaminoazotoluene, and *p*-bromobenzeneazodimethylaniline generally yield violet salts; dibromotolueneazodimethylaniline and tribromobenzeneazodimethylaniline give chiefly orange salts, whilst about equal numbers of violet and orange salts are obtained from *p*-aminoazobenzene.

A slight change in the constitution of the aminoazo-compound is sufficient to produce a change in the colour of the salt with the same acid; thus formylaminoazobenzene hydrochloride is orange, whereas the corresponding acetyl compound is violet.

In many cases the same salt has been obtained in the two forms; generally, the orange, labile variety is first precipitated, usually in the form of very thin leaflets, which then more or less readily changes into the violet, stable form, crystallising as a rule in needles. Mixed crystals of the two forms have not been observed.

The orange salts are undoubtedly azo-compounds having the formula $Ph\cdot N:N\cdot C_6H_4\cdot NR_2,HX$, since they possess almost the same colour and absorption spectrum as azobenzene and azobenzenetrimethylammonium salts, all of which are orange, since they do not contain a mobile hydrogen atom. On the other hand, the violet salts, since they are also unimolecular, must be isomeric with the orange salts, and must consequently have a quinonoid structure. Attempts to prepare unchangeable representatives of the form

$$Ph\cdot NR\cdot N:C_6H_4:NMe_2R$$

were unsuccessful; nevertheless, a violet solution of a very unstable base, obtained from phenylmethylhydrazine and benzoquinonimine, which must have the formula $NMePh\cdot N:C_6H_4:NH$, showed the same absorption spectrum as the violet salts.

The orange salts do not change spontaneously at the ordinary temperature into the violet forms, but frequently when heated or crushed. Solutions of the salts contain the two forms in a state of equilibrium, depending largely on the nature of the solvent. Chloroform and indifferent solvents favour the violet form, whilst acetone, alcohol, and ether favour the orange form; for example, the solution of the orange diethylaminoazobenzene hydrochloride in acetone is yellow, whilst in chloroform it is violet; nevertheless, the orange salt is precipitated on adding ether to the chloroform solution.

The following salts were obtained either by adding an ethereal solution of the aminoazo-compound to an excess of acetyl haloid, or by adding a solution of the compound in alcohol or glacial acetic acid to an excess of an aqueous solution of the acid.

p-*Aminoazobenzene hydrobromide*, *hydriodide*, and *perchlorate* are violet; the *nitrate* is flesh-red, becoming violet when pulverised;

the yellow *sulphate* is very stable, and changes very slowly into the violet form when powdered; the *hydrogen sulphate* is violet; the *oxalate* forms yellow leaflets, and changes into the violet form when heated under paraffin at 100°; the *dithionate* forms flesh-coloured leaflets; the *toluenesulphonate* and *benzenesulphinate* are yellow; the *trichloroacetate* is violet.

p-*Dimethylaminoazobenzene hydrochloride, hydrobromide, hydriodide, sulphate, perchlorate, nitrate, oxalate, trichloroacetate,* and *toluenesulphonate* are violet. A solution of the yellow oxalate is obtained by mixing the dry base and anhydrous oxalic acid in absolute ethereal solution; the solid salt was not isolated.

p-*Diethylaminoazobenzene* forms golden-yellow crystals, m. p. 95°; the *hydrochloride* and *hydrobromide* are orange-yellow. Only violet salts of *p*-anilinoazobenzene were obtained. *Formylaminoazobenzene hydrochloride* is flesh-coloured; the *sulphate* is yellow. *Acetylaminoazobenzene hydrochloride* is carmine-red; the *hydrobromide* when dry is carmine-red, but when moistened with ether is violet; the yellow *sulphate* turns violet when powdered.

p-*Tolueneazo*-o-*toluidine hydrochloride* is carmine-red; the *sulphate* and *oxalate* are orange; the *nitrate* is violet; the *dithionate* and *toluenesulphonate* are flesh-coloured; the *iodate* is carmine-red; the *benzenesulphinate* forms orange needles, which when lightly pressed turn violet, often becoming again orange after some time.

Tolueneazodimethylaniline hydrochloride, hydrobromide, sulphate, nitrate, iodate, and *toluenesulphonate* are violet; the *benzenesulphinate* is obtained as a brown precipitate, which quickly turns violet.

Benzeneazo-2 : 6-dibromoaniline has m. p. 191° (Berju gives m. p. 152°; Abstr., 1884, 1148); the *hydrochloride* and *sulphate* are violet.

p-*Bromobenzeneazodimethylaniline hydrochloride, hydrobromide, sulphate,* and *nitrate* are violet.

Dibromotolueneazodimethylaniline, $C_7H_5Br_2\cdot N{:}N\cdot C_6H_4\cdot NMe_2$, crystallises in orange needles, m. p. 156°; the *hydrochloride, hydrobromide, sulphate, iodate,* and *toluenesulphonate* are yellow or orange. *Tribromobenzeneazodimethylaniline hydrochloride* and *hydrobromide* are bright orange; violet salts of the last two bases could not be obtained.

W. H. G.

Crystalline Egg-Albumin. EDITH G. WILLCOCK (*J. Physiol.*, 1908, **37**, 27—36).—The specific rotation of crystallised egg-albumin is about −31°; this is a little higher than Hopkins gave, and the result is due to a modification in the method of estimating the protein in solution. Small variations noted are believed to be due to the formation of varying protein-acid substances. If ammonium sulphate is used as the agent in crystallisation, it can be replaced by magnesium sulphate in recrystallisation without affecting the character of the crystals. The dialysed albumin is acid to litmus, but the protein part moves to the cathode and is thus basic. The hypothetical protein-acid can form salts with a weak base. There is some evidence for association with the precipitating salt. The percentage of sulphur in crystallised egg-albumin is 1·324.

W. D. H.

Behaviour of Oxyhæmoglobin towards Reducing Agents. Gustav Hüfner (*Chem. Zentr.*, 1908, i, 739; from *Arch. Anat. Physiol.*, 1907, 463—465).—The reduction of oxyhæmoglobin seldom proceeds quantitatively; generally, secondary reactions take place, whereby part of the loosely combined oxygen is liberated, oxidising not only other organic substances, but the molecule of the colouring material itself. J. V. E.

The Influence of Light on the Formation of Carboxymethæmoglobin. A. Gröber (*Arch. exp. Path. Pharm.*, 1908, 58, 343—349).—Carboxyhæmoglobin is more rapidly converted into the methæmoglobin derivative by potassium ferricyanide in the presence of light than in darkness, or in light deprived of the more active chemical rays. S. B. S.

Hæmin. A. von Siewert (*Arch. exp. Path. Pharm.*, 1908, 58, 386—396).—Hæmin can be prepared by coagulating a solution of red blood corpuscles by heat in the presence of acetic acid, partly drying the coagulum in air, making the latter into a thin paste with alcohol, then adding a small quantity of 10—15% potassium hydroxide solution to the paste, and finally acidifying the viscous solution thus obtained with sulphuric acid; the protein is thereby precipitated and the hæmatin remains in solution. From the latter, by suitable treatment with hydrochloric acid, hæmin can be obtained. The hæmin can be purified by dissolving in dilute sodium hydroxide solution, adding barium hydroxide solution in excess, and treating the barium precipitate thus produced with alcoholic sulphuric acid; the barium sulphate is then filtered off, and alcoholic hydrochloric acid is added to the filtrate at 70°; after a time, the hæmin hydrochloride separates in crystalline form. In addition to the ordinary hæmin, another substance can be prepared, which differs from hæmin in that it is insoluble in sodium hydroxide. This can be obtained by treating the coagulated blood powder (see above) with 95% alcohol containing 1 volume per cent. sulphuric acid and adding alcoholic hydrochloric acid to the solution thus obtained. A mixture of the crystals of hæmin and the alcohol-insoluble substance separates out. The analyses indicate that the latter is an anhydride of the former. The hæmin preparations obtained by the above methods gave, on analysis, numbers agreeing with those previously obtained by Küster. S. B. S.

Non-existence of Urocarmine as a New and Definite Colouring Matter. Louis C. Maillard (*J. Pharm. Chim.*, 1908, [vi], 27, 427—437).—Largely polemical. The author maintains that Florence's urocarmine (*ibid.*, 147) is only an impure form of indirubin. When a chloroform solution of urocarmine, prepared according to Florence's directions, is extracted with a 1% sodium hydroxide solution, a bright yellow colouring matter is removed, which is not urobilin, since it shows no fluorescence when treated with an alcoholic solution of zinc chloride or acetate, with or without the addition of ammonia.

If the chloroform solution after treatment with alkali is washed with dilute acid and with water, evaporated to dryness, and the residue extracted with ether, the ethereal solution has an absorption spectrum identical with that of indirubin, and on evaporation gives a residue having all the characteristics of the latter colouring matter and no longer possessing the tarry appearance of urocarmine.

Removal of the indirubin, which forms the greater part of the chloroform extract, leaves a brownish-black residue. Alcohol extracts a small quantity of indigo-brown from the latter, and leaves a little indigotin. Thus it is shown that urocarmine is a mixture of at least four substances, two of which are definite compounds.

The author suggests that uronigrin is really indigo-brown.

E. H.

The Carbohydrate Group in the Nucleic Acid. Hermann Steudel (*Zeitsch. physiol. Chem.*, 1908, **55**, 407—411).—An attempt was made to isolate the reducing group of nucleic acid by treating the sodium salt of the α-acid prepared from thymus with an aqueous extract of thymus gland, which contains a ferment in the presence of which nucleic acids undergo hydrolysis with the scission of phosphoric acid and the alloxuric bases. By this means, only incomplete hydrolysis takes place, and there was evidence of the scission of a reducing substance. The latter was not fermented by yeast, neither could a phenylhydrazine derivative be obtained from it. On hydrolysis with nitric acid, a reducing substance was also obtained, which appeared to be in combination with phosphoric acid (the greater part of which was in organic combination at the end of the experiment). S. B. S.

Guanylic Acid of the Spleen. Walter Jones and L. G. Rowntree (*J. Biol. Chem.*, 1908, **4**, 289—296).—A true guanylic acid in Bang's sense is obtainable, not only from the pancreas, but also from the spleen nucleoprotein. It is regarded as probable that most nucleic acids yield a similar substance in addition to adenylic acids. Odenius (Maly's *Jahresb.*, 1900, **39**) has prepared it from the mammary gland. The character of guanylic acid relied on for its identification is the fact that it does not yield adenine. The pentose and glycero-phosphoric acid which Bang states are obtainable from guanylic acid do not appear to have been sought for. W. D. H.

The Protein Peptones. III. Felix Rogozinski (*Beit. chem. Physiol. Path.*, 1908, **11**, 229—240).—The hydrolysis products of the *Ab* phenylcarbimide fraction previously obtained by Raper (this vol., i, 266) were investigated. The following substances were isolated: a base, m. p. 231—233°, histidine, arginine, glutamic acid, aspartic acid, leucine, tyrosine, aniline, ammonia, and a nitrogen-free substance, m. p. 99—101°. Also the following substances, which were characterised only by qualitative reactions: proline, phenylalanine, and valine or *iso*leucine. The *Ab* fraction differs from Raper's *Ac* fraction in that the latter contains lysine. S. B. S.

The Protein Peptones. IV. Felix Rogozinski (*Beit. chem. Physiol. Path.*, 1908, **11**, 241—254).—The peptones obtained by tryptic digestion of the blood proteins were investigated. The coagulable proteins were separated by heating; the filtrate was saturated with ammonium sulphate, and to the filtrate from the precipitate thus obtained, iron ammonium alum in saturated ammonium sulphate solution was added. After filtering off the resulting precipitate and freeing the liquid from iron by means of hydrogen sulphide, a liquid was obtained which, after saturation with more ammonium sulphate and acidification with dilute sulphuric acid (saturated with ammonium sulphate), gave a precipitate with potassium mercuric iodide solution prepared by Raper's method. The latter precipitate yielded four fractions: (1) a fraction insoluble in 10% potassium iodide, (2) a fraction soluble in water, (3) a fraction soluble in 5% ammonium carbonate, and (4) a fraction soluble in 20% ammonia. The condensation products with phenylcarbimide were prepared from these fractions. From fractions (2) and (3), sub-fractions differing in the solubility of their barium salts could be obtained. It was noticed that the quantity of iron ammonium alum precipitate diminished with a lengthened period of tryptic digestion. Some of the fractions obtained by tryptic digestion appear to be identical with fractions obtained by Raper by similar methods from the products of peptic digestion. S. B. S.

Tryptophan. EMIL ABDERHALDEN and LOUIS BAUMANN (*Zeitsch. physiol. Chem.*, 1908, 55, 412—415).—Tryptophan was shown by Abderhalden and Kempe to have the specific rotation in *N*-sodium hydroxide solution of $+5{\cdot}7°$ to $+6{\cdot}3°$. The correctness of these numbers has been confirmed. In aqueous solution, $[\alpha]_D^{20}$ $-30{\cdot}33°$, which is not far removed from that given by Hopkins and Cole ($-33°$). This fact, perhaps, justifies the designation of tryptophan obtained by the digestion of proteins as the *l*-tryptophan. It can be readily racemised, especially by recrystallisation from pyridine. It is generally found in combination with another substance, *hydroxytryptophan*, $[\alpha]_D^{20}$ $-11{\cdot}19°$. The last two facts may account for the varying numbers given for the specific rotation by various observers.

S. B. S.

Protamine as a means of Distinguishing Primary from Secondary Proteoses. ANDREW HUNTER (*Proc. physiol. Soc.*, 1908, v—vi; *J. Physiol.*, 37).—Protamine precipitates other proteins, but protone does not. It also precipitates primary proteoses, but not secondary proteoses, peptones, or polypeptides. W. D. H.

Protagon. OTTO ROSENHEIM and M. CHRISTINE TEBB (*Proc. physiol. Soc.*, 1908, i—iv; *J. Physiol.*, 37).—A continuation of the discussion with Cramer; fresh proofs are adduced that protagon is a mixture. An artificial mixture of its constituents manifests the same properties, including specific rotatory power, as "natural protagon."

W. D. H.

The Course of the Fermentative Degradation of Polypeptides. V. EMIL ABDERHALDEN and ARTHUR H. KOELKER (*Zeitsch. physiol. Chem.*, 1908, 55, 416—426).—The following polypeptides were investigated: *d*-alanylglycine, $[\alpha]_D + 50°$; *d*-alanylglycylglycine, $[\alpha]_D + 30°$, and *d*-alanylglycyl-glycylglycine, $[\alpha]_D + 22{\cdot}4°$. The rate of change was measured by observing the changes in the optical rotation of the solutions under the influence of various proteoclastic ferments, as the hydrolysis products are either inactive or have very different rotations to the original polypeptide. Parallel experiments were carried out (*a*) with constant quantities of ferment and varying quantities of polypeptide, and (*b*) with constant quantities of polypeptide and varying quantities of ferment. The results indicate that in most cases *d*-alanine is the first product of hydrolysis. It is possible that by the method of experiment described, a process may be evolved for the standardisation of enzymes. S. B. S.

Action of the Juices Expressed from Cells on Polypeptides. EMIL ABDERHALDEN and FILIPPO LUSSANA (*Zeitsch. physiol. Chem.*, 1908, **55**, 390—394).—As an extension of previous work, the action of the expressed sap from the cells of the lense and of brain substance was investigated. The former splits *dl*-alanylglycine, glycyl-*l*-tyrosine, diglycylglycine, but only slightly glycyl-*dl*-alanine, into their component amino-acids. The latter juice splits only two of the four dipeptides, namely, *dl*-alanylglycine and diglycylglycine.

W. D. H.

Action of the Juice of Psalliota campestris on Polypeptides. EMIL ABDERHALDEN and AUGUSTE RILLIET (*Zeitsch. physiol. Chem.*, 1908, **55**, 395—396).—The juice obtained at high pressures from this mushroom splits *dl*-alanylglycine, *dl*-leucylglycine, and diglycylglycine into their component amino-acids. Experiments were also tried with glycyl-*l*-tyrosine, but its decomposition products could not be separated; they are possibly destroyed by a ferment allied to tyrosinase. The results, however, are incomplete, owing to lack of material. W. D. H.

The Activity of Trypsin and a Simple Method for its Estimation. ERNST FULD (*Arch. exp. Path. Pharm.*, 1908, **58**, 468).—A claim for priority (compare Gross, this vol., ii, 234).

S. B. S.

Adsorption of Tryptase by Solids. EDUARD BUCHNER and FRITZ KLATTE (*Biochem. Zeitsch.*, 1908, **9**, 436—438).—The following substances were found, after immersion in trypsin solution, to have adsorbed the ferment: fibrin, silk, wool, and cotton threads, linen, paper, agar-agar strips, asbestos, and glass wool. They possessed the power, after removal from the solution, of liquefying gelatin. From the glass wool, the ferment could be readily removed by washing.

S. B. S.

Hydrolytic Enzyme in the Resting Seeds of some Gramineæ. YOSHIO TANAKA (*J. Coll. Eng. Tokyo*, 1908, **4**, 39—52).—The optimum temperature for millet diastase is higher than that of barley diastase, being 50—55°. Millet diastase further differs from that of barley and of other cereals in rapidly liquefying starch to dextrins without producing much maltose until the dextrins have all been converted into achroodextrin. When diastase from millet acts on the glutinous starch of the same plant (*Setaria italica*), the rapid liquefaction and slow saccharification is even more apparent than with ordinary starch. The name α-erythrodextrin is suggested for a substance coloured red by iodine and very resistant to millet diastase. A mixture of millet and barley diastases acts much more vigorously than either diastase alone. G. B.

Oxidation Processes in the Living Cell. ALEXIS BACH and ROBERT CHODAT (*Bied. Zentr.*, 1908, **37**, 168).—A résumé of the authors' work on this subject (Abstr., 1902, ii, 344, 522; 1903, i, 219, 377, 378, 671; 1904, i, 359, 542, 792). E. J. R.

Some Artificial Peroxydiastases; the Important Rôle of Iron in Their Action. JULES WOLFF (*Compt. rend.*, 1908, **146**, 781—783).—The author has indicated previously (this vol., i, 137) the resemblance between the action of certain iron salts and that of the peroxydiastases (name proposed by Bertrand instead of peroxydases). It is now shown that the properties of certain colloidal compounds of iron are practically identical with those of the peroxydiastases. Colloidal ferrous ferrocyanide solution (containing 10 mg. of iron per litre), obtained by interaction of very dilute solutions of an alkali ferrocyanide and a ferrous salt, produces all the reactions of the peroxydiastases. When added to a saturated solution of quinol containing traces of hydrogen peroxide, the reagent gives crystals of quinhydrone in one to two minutes. The action is considerably retarded by traces of ferrous or ferric sulphates, and very small quantities of these salts are sufficient to prevent entirely the formation of quinhydrone. Potassium ferrocyanide has no appreciable effect. Ferric ferrocyanide and ferrous and ferric ferricyanides have an analogous, but smaller, diastatic activity. This artificial peroxydiastase resembles the natural substances also in the following properties. It can be filtered through paper without alteration, but is rendered inactive by filtration through collodion, and it loses part of its activity by one minute's boiling. Traces of mineral acids retard its action, and excess of hydrogen peroxide has the toxic effect discovered by Bach and Chodat (Abstr., 1904, i, 542, 792) for natural peroxydiastases.

In two solutions containing 1 gram of pyrogallol, the amount of hydrogen peroxide corresponding with 28 c.c. of active oxygen, and a quantity of colloidal ferrocyanide equivalent to 0·00004628 gram of iron, to one of which all the hydrogen peroxide was added at first, whilst to the other, half was added at the beginning and the remainder after two hours, the quantities of purpurogallin formed in twenty-four hours were (1) 0·065 gram and (2) 0·123 gram, or 1400 times and 2657 times respectively the weight of iron present. The action was still vigorous after twenty-four hours. E. H.

Proof, by means of the Chromogram Method, that Hydrogenase takes an Active Part in Alcoholic Fermentation. J. Grüss (*Ber. Deut. bot. Ges.*, 1908, **26a**, 191—196).—A method is indicated, but not as yet described in detail, by means of which the various enzymes contained in plant juices can be identified separately. A drop of the juice is placed on filter paper, when, owing to unequal adsorption by the paper, the enzymes are distributed in various zones and may be identified by colour reactions (thus yielding a "chromogram").

By means of this method, it is shown that, when yeast-juice is added to dextrose solution and powdered sulphur, hydrogenase causes the production of hydrogen sulphide. G. B.

Can the Existence of an Anticatalase be Demonstrated? H. De Waele and Albert J. J. Vandevelde (*Biochem. Zeitsch.*, 1908, **9**, 264—274).—The catalases used in these experiments were dilute sterile solutions of laked blood. The amount of hydrogen peroxide destroyed at 25° in two hours by the catalases was determined in the presence of various normal sera and antisera produced by the injection of the catalases into different animals. The formation of anticatalases by the methods generally employed in investigations on immunity could not be demonstrated. S. B. S.

The Action of the Electric Current on Yeast-juice. Friedrich Resenscheck (*Biochem. Zeitsch.*, 1908, **9**, 255—263).—Experiments were made to determine whether the active substances of the yeast-juice wander to either cathode or anode during the passage of an electric current. It was found that the activity of the solution round the cathode slightly increased, whereas that round the anode slightly diminished, when the time of passage was short (one to three hours). After six hours, the activity round both anode and cathode was diminished. S. B. S.

Action of Beer Yeast on Acid Amides. Jean Effront (*Compt. rend.*, 1908, **146**, 779—780).—Ehrlich has shown (Abstr., 1907, i, 592) that beer yeast has the property of splitting racemic amino-acids, forming amyl alcohol from leucine. The author finds that yeast contains a diastase *amidase* which decomposes acid amides, giving ammonia and volatile acids. A solution containing 2 grams of asparagine, 10 grams of yeast, and 6 c.c. of *N*-soda in 100 c.c. of water is maintained at 40°; samples removed at intervals, and the ammonia estimated by distillation with magnesia. The amounts of ammonia found indicate that decomposition occurs to the extent of 50% in forty-eight hours, and is complete in seventy-two hours. Control experiments in which (1) asparagine and alkali are present without yeast, and (2) yeast and soda are present but no asparagine, give only trifling amounts of ammonia in seventy-two hours. After sixty hours, the liquid contains the enzyme, amidase, and, if filtered, 100 c.c. of it will completely decompose 1 gram of asparagine in six hours, but the filtrate completely loses its activity when heated at 90°. The diastatic nature of the action of the yeast is confirmed by the proportionality between the time and the quantity of amide transformed. The active substance of autolysed yeast acts also on aspartic acid, leucine, and glutamic acid. The optimum temperature for its action is 40—45°; alkalis favour, and acids retard, the action. Ten grams of asparagine decomposed by the enzyme gave 5·5 grams of acids, b. p. 110—145°, in which propionic acid was recognised.

The enzyme is invariably present in top-fermentation and aerobic yeasts, and it has been observed in *Amylobacter butylicus*. Its presence in bottom-fermentation yeasts is uncertain. E. H.

Stability of Atoxyl. W. L. YAKIMOFF (*Chem. Zentr.*, 1908, i, 979; from *Deutsch. med. Woch.*, 1908, **34**, 200—202).—Dilute atoxyl solutions kept in the dark remain unaltered for some time, although fresh solutions are to be preferred. The stock solution should be made with cold boiled water, stored unsterilised, and screened from the light. Before use, the stock solution must be boiled for one to two minutes. The solution should not be allowed to become alkaline.

J. V. E.

Primary Aromatic Arsonic Acids. OSCAR ADLER and RUDOLF ADLER (*Ber.*, 1908, **41**, 931—934).—Béchamp's method (*Compt. rend.*, 1863, **56**, i, 1173; Ehrlich and Bertheim, Abstr., 1907, i, 812) of preparing *p*-aminophenylarsonic acid by heating aniline arsenate appears to be a general one for the production of primary aromatic arsonic acids; practically, it is more convenient to heat arsenic acid with an excess of the primary amine at 200°.

2-*Aminotolyl*-5-*arsonic acid*, $NH_2\cdot C_7H_6\cdot AsO(OH)_2$, is purified most readily by conversion into the *sodium* salt, $C_7H_9O_3NAsNa$, which forms colourless crystals. By treatment with acetic anhydride, it yields an *acetyl* derivative, $NHAc\cdot C_7H_6\cdot AsO(OH)_2$, which is oxidised by alkaline potassium permanganate to 2-*acetylamino*-1-*carboxyphenyl*-5-*arsonic acid*, $NHAc\cdot C_6H_3(CO_2H)\cdot AsO(OH)_2$. The amino-compound resulting from the hydrolysis of the preceding acid is converted by the diazo-reaction into 2-*hydroxy*-1-*carboxyphenyl*-5-*arsonic acid*, $OH\cdot C_6H_3(CO_2H)\cdot AsO(OH)_2$, which crystallises in colourless needles.

Aminonaphthylarsonic acid, $NH_2\cdot C_{10}H_6\cdot AsO(OH)_2$, prepared from α-naphthylamine and α-naphthylamine arsenate at 200°, is purified through the sodium salt, and is converted by the diazo-reaction into *hydroxynaphthylarsonic acid*, which crystallises in colourless needles.

C. S.

Chemistry of Silicon. ALBERT LADENBURG (*Ber.*, 1908, **41**, 966).—The barium triphenylsilicoltrisulphonate described previously (Abstr., 1907, i, 668) is not pure, and contains 3·3% Si instead of 3·9%.

J. J. S.

Organic Chemistry.

Exact Analysis of Marsh Gas. Dissociation of Several Hydrocarbons Effected in the Eudiometer for Measuring Fire-damp. Nestor Gréhant (*Compt. rend.*, 1908, **146**, 1199—1200).—A sample of gas collected at the bottom of a shaded pool of water contained 67·7% of methane.

Samples (60 c.c.) of methane, ethylene, and acetylene were introduced respectively into three of the author's eudiometers for measuring fire-damp ("eudiomètre-grisoumètre"), in which spirals of platinum wire are suspended. When these spirals are made red-hot by passing an electric current through them 500—600 times, the methane dissociates gradually, expanding to twice its original volume, hydrogen being liberated and a small amount of carbon deposited ; the ethylene gives some small drops of tar, deposits carbon on the walls of the vessel, and increases slightly in volume, whilst the acetylene inflames at the first passage of the current, giving an abundant deposit of carbon on the spiral and on the eudiometer walls, and decreasing considerably in volume. E. H.

Diethyl*iso*propylmethane [β-Methyl-γ-ethylpentane]. Latham Clarke (*Amer. Chem. J.*, 1908, **39**, 572—579).—In an earlier paper (Abstr., 1907, i, 169) an account has been given of the preparation of a new octane (δ-methylheptane). Another octane, β-methyl-γ-ethylpentane (diethyl*iso*propylmethane), has now been synthesised by two different methods.

γ-Ethyl-β-pentanone (diethylacetone), on treatment with magnesium methyl iodide, yields *β-methyl-γ-ethyl-β-pentanol*, $OH·CMe_2·CHEt_2$, b. p. 156°/760 mm., which has a strong aromatic odour. On treating this compound with iodine and red phosphorus, *β-iodo-β-methyl-γ-ethylpentane*, $CMe_2I·CHEt_2$, is obtained, which on reduction with zinc and hydrochloric acid is converted into β-methyl-γ-ethylpentane.

*Ethyl ethyl*iso*propylacetoacetate*, $CH_3·CO·CEtPr^{\beta}·CO_2Et$, b. p. 224°/760 mm., prepared by Conrad and Limpach's method (Abstr., 1878, 781), is a colourless liquid with a pleasant pine-wood-like odour. On hydrolysis with potassium hydroxide, it yields γ-iso*propyl-β-pentanone* (*ethyl*iso*propylacetone*), $CH_3·CO·CHEtPr^{\beta}$, b. p. 154°/760 mm., a colourless liquid with a camphor-like odour, which on reduction with sodium in the presence of ether and water furnishes γ-iso*propyl-β-pentanol*, $OH·CHMe·CHEtPr^{\beta}$, b. p. 172°/760 mm., a colourless, oily liquid with an odour like that of sour bread. This substance is converted into *β-iodo-γ-*iso*propylpentane*,

$$CHMeI·CHEtPr^{\beta},$$

which on reduction yields β-methyl-γ-ethylpentane, identical with the product obtained by the preceding method.

β-Methyl-γ-ethylpentane (*diethyl*iso*propylmethane*), $CHMe_2·CHEt_2$, b. p. 114°/760 mm., is a nearly colourless liquid, with D^{15} 0·7084 and $[n]^{25}_{D}$ 1·3996. E. G.

Behaviour of Fats and Oils towards Calcium Carbonate. A. Künkler and H. Schwedhelm (*Chem. Zentr.*, 1908, i, 1322; from *Seifensieder-Zeit.*, 1908, **35**, 165—166).—With the object of throwing light on the origin of petroleum and mineral waxes, the behaviour of fast, oils, waxes, and resins with chalk, common salt, and clay has been investigated. The results indicate the intermediate formation of a calcium salt and a ketone; the latter, especially in the presence of a contact substance like chalk, loses part of its oxygen, probably as water, at moderate temperatures, and as carbon monoxide or carbon dioxide at high temperatures. In these circumstances, it becomes possible to explain the optical activity and high viscosity of these natural oils by the carbon of the keto-group becoming asymmetric in the presence of mixed ketones, and by the formation of complex molecules with branching chains and having high viscosity. As explaining the fact that large quantities of carbon dioxide do not occur with natural oils, it is stated that the elimination of oxygen from the fatty acids only takes place on or near the surface of the earth. J. V. E.

Catalytic Dehydration of Organic Compounds. Jean B. Senderens (*Compt. rend.*, 1908, **146**, 1211—1213. Compare this vol., ii, 166).—The author has extended his work on the dehydration of organic compounds by means of gently-calcined alumina. At 300°, ethyl ether is decomposed into water and ethylene; this is a good method of preparation of the latter gas. Acetic acid at 350° gives acetone, water, and carbon dioxide. Propionic acid is similarly decomposed with formation of diethyl ketone. Ethyl acetate is acted on at 350° according to the equation

$$2CH_3\cdot CO_2Et = H_2O + 2C_2H_4 + CO_2 + CH_3\cdot CO\cdot CH_3.$$

Ethyl oxalate is decomposed as follows:

$$C_2O_4Et_2 = H_2O + CO_2 + CO + 2C_2H_4$$

Alumina can also effect the removal of 1 mol. of a halogen hydride; thus, at 250°, chloro*iso*butane yields *iso*butylene, chloropropane gives propylene, and ethylene dichloride at 350° furnishes vinyl chloride. Glycerol gives acraldehyde and polyglycerols, and oxalic acid is completely transformed into water and carbon mon- and di-oxide. In all cases, heat alone has no action at the temperatures used. J. C. C.

Mixed Trihalogen Derivatives of Methane. Victor Auger (*Compt. rend.*, 1908, **146**, 1037—1039).—In the preparation of dichloroiodomethane by the action of mercuric chloride on iodoform (Serullas, *Ann. Chim. Phys.*, 1827, [ii], **34**, 97; Bouchardat, *Annalen*, 1837, **22**, 233), *chlorodi-iodomethane*, HCl_2Cl, is also formed. Thus distillation under 100 mm. pressure of an intimate mixture of 700 grams of mercuric chloride and 1100 grams of iodoform gives 235 grams of pure dichloroiodomethane, $CHCl_2I$, b. p. 40°/30 mm., 131°/760 mm., D^0 2·41, and 323 grams of *chlorodi-iodomethane*, $CHClI_2$, a colourless liquid, m. p. −4°, b. p. 88°/30 mm., 200°/760 mm. (decomp.), D^0 3·17, which is very unstable in the presence of air and light, becoming rapidly coloured violet. It is decomposed by water in the presence of air, giving carbonyl chloride and probably the compound $COClI$.

The product obtained by Bouchardat (*loc. cit.*) by the action of bromine on iodoform was a mixture of bromoform and iodine (Löscher, Abstr., 1888, 436), not, as this author thought, dibromoiodomethane, $CHIBr_2$. The latter can be readily prepared by distilling under 150 mm. a mixture of equal parts of iodoform and mercuric bromide. *Dibromoiodomethane*, $CHBr_2I$, is a white, crystalline solid, m. p. 22·5°, b. p. 101—104°/50 mm., 91°/42 mm. In the solid state it is stable towards light, but its solutions are very unstable in the presence of air. Bromine converts it even at 0° into bromoform. In the preparation, *bromodi-iodomethane*, $CHBrI_2$, is also formed, but cannot be isolated in a pure state; it is readily prepared by the action of cold bromine on iodoform dissolved in carbon tetrachloride, when a mixture of the isomerides is formed which can be separated by fractional crystallisation. Bromodi-iodomethane forms yellow, hexagonal crystals, m. p. 60°, b. p. 110°/25 mm., unchanged by light when in the solid state, but very unstable in solution. E. H.

Catalytic Dehydration of Alcohols by Calcium Sulphate and by Aluminium Silicate. Jean B. Senderens (*Bull. Soc. chim.*, 1908, [iv], 3, 633—638).—A continuation of work on the dehydration of alcohols by heated inorganic materials (compare Abstr., 1907, ii, 248; i, 577; 1908, ii, 166). Gypsum, dehydrated by careful calcination, and also "plaster of Paris" begin to decompose ethyl alcohol at 370° and dehydrate it rapidly at 420°, yielding a gas containing over 90% of ethylene, the rest being hydrogen. Anhydrite does not decompose ethyl alcohol below 460°, and then only slowly, yielding a gas containing 85·7% of hydrogen and 14·3% ethylene. Gypsum, which has been calcined at a red heat during three hours, approaches anhydrite in its behaviour, acting on alcohol slowly at 485°, and yielding a gas containing 71·2% of hydrogen. These results are explained by assuming that the dehydration is due to the formation of temporary hydrates of the sulphate, and the tendency of the latter to form hydrates is diminished, probably as the result of change in molecular structure, either by heating at a high temperature during a short period or at a low temperature over a long period. In confirmation of this, it is pointed out that finely-powdered gypsum, not previously dehydrated, at first decomposes alcohol rapidly at 420—430°, and as the heating is continued, the rate falls to 17% of its initial value in the course of ten hours. Aluminium silicate, "modelling clay," and "white clay" also decompose alcohol rapidly at 420°, and, unlike calcium sulphate, their efficiency does not change as the result of their being previously calcined. The gas produced contains 94—98% of ethylene. Kaolin decomposes alcohol slowly at 370°, and more readily at 420°, yielding in the two cases gases containing 87% and 93·5% of ethylene respectively. After being calcined at a red heat, it approaches aluminium silicate and the clays mentioned above in efficiency. The presence of iron oxide or calcium carbonate in the clays modifies their action, and gives rise to a mixture of gases richer in hydrogen.

T. A. H.

Studies in Steam Distillation and the Recovery of Amyl Alcohol from the Acid Liquors obtained in the Gerber Process. H. Droop Richmond (*Analyst*, 1908, 33, 209—217).—In the first part of this paper the author deals with steam distillation from a mathematical and theoretical point of view, whilst in the second part, the results of experiments on the recovery of amyl alcohol from the acid liquid obtained in the Gerber process of estimating fat in milk are described. It appears that a preliminary steam distillation of these liquids yields a crude amyl alcohol, which must be further purified by fractionation before a product boiling at 123—131° is obtained which is suitable for use again in the Gerber process. The readings observed when this recovered amyl alcohol is employed show an excess of about 0·05%. W. P. S.

Hydrate and Iodo-derivatives of Propargyl Alcohol (Propinol). Robert Lespieau (*Bull. Soc. chim.*, 1908, [iv], **3**, 638—640). —An extension of previous work on propargyl alcohol and some of its derivatives (Abstr., 1898, i, 116; 1899, i, 184). In previous papers it was stated that this alcohol crystallises at $-17°$. The substance which separates in this way is a *monohydrate*, C_3H_4O,H_2O. *Propargyl phenylurethane* crystallises from benzene on addition of light petroleum, and has m. p. 62—63°. Iodopropargyl alcohol, $CI\vdots C\cdot CH_2\cdot OH$, previously described (Abstr., 1899, i, 184), changes in part when kept or when treated with boiling water into tri-iodoallyl alcohol, $CI_2{:}CI\cdot CH_2\cdot OH$, which is more readily obtained by adding iodine solution in slight excess to the copper derivative of propinol, suspended in potassium iodide solution and kept at 100°, and may be used for the characterisation of propargyl alcohol; *tri-iodoallyl acetate*, m. p. 41—41·5°, crystallises from acetic acid. T. A. H.

Propargylcarbinol. Robert Lespieau and Pariselle (*Compt. rend.*, 1908, **146**, 1035—1037).—By passing a slow current of hydrogen bromide through methyl $\gamma\delta$-dibromobutyl ether,

$$CH_2Br\cdot CHBr\cdot[CH_2]_2\cdot OMe$$

(Abstr., 1907, i, 580), kept at 100° until methyl bromide ceases to be evolved, cooling the product to 0°, saturating with hydrogen bromide, and heating in a sealed tube at 100° for ten hours, *$\alpha\beta\delta$-tribromobutane*, $CH_2Br\cdot CHBr\cdot[CH_2]_2\cdot Br$, a liquid, b. p. 112—113°/13 mm., is formed. When this is heated to boiling with 20% by weight of solid potassium hydroxide, it is partly transformed into a *dibromobutylene*, b. p. 57—60°/14 mm., to which the authors ascribe the formula $CH_2{:}CBr\cdot[CH_2]_2\cdot Br$.

If the action of the potash is carried too far, acetylenic compounds are produced. *β-Bromo-Δ^{α}-butene-δ-ol*, $CH_2{:}CBr\cdot CH_2\cdot CH_2\cdot OH$, a liquid, b. p. 69—72°/11 mm., 175°/760 mm. (decomp.), is formed by the saponification of the corresponding *acetin*, a liquid, b. p. 75—78°, which results from the action of potassium acetate on $\beta\delta$-dibromo-Δ^{α}-butylene. When β-bromo-Δ^{α}-butene-δ-ol is acted on by a 50% solution of potassium hydroxide, *butinol*, $CH\vdots C\cdot CH_2\cdot CH_2\cdot OH$, a liquid, b. p. 133—136°/760 mm., is formed. This gives a *phenylurethane*, m. p. 66—67°. By treating butinol with an ammoniacal cuprous chloride solution, a yellow precipitate is formed, which, when suspended in a solution of iodine in potassium iodide and gradually heated at 100°, is converted into *$\alpha\alpha\beta$-tri-iodo-Δ^{α}-butene-δ-ol*, $CI_2{:}CI\cdot CH_2\cdot CH_2\cdot OH$, a substance, m. p. 112—113°, which becomes rose-coloured on exposure to light, and gives an *acetyl* derivative, m. p. 51—52°. E. H.

Alkylene Glycol-chlorohydrin Ethers and Tiffeneau's Wandering of Phenyl. PAUL HOERING (*Ber.*, 1908, **41**, 1889—1893).—A reply to Houben (this vol., i, 307). G. Y.

New Method for the Preparation of Diamyl Ether and Ethers of the Higher Alcohols. GEORG SCHROETER and WALTER SONDAG (*Ber.*, 1908, **41**, 1921—1925. Compare Schroeter and Herzberg, Abstr., 1905, i, 85; Krafft and Roos, Abstr., 1892, 1219).—Large amounts of methyl ether are formed when methyl alcohol is heated with methionic acid at 120° under pressure, whilst ethyl ether and water distil continually when ethyl alcohol is run into a mixture of ethyl alcohol and methionic acid at 140°, the methionic acid being afterwards regained unchanged. Amyl and higher ethers are readily prepared by heating the corresponding alcohols with small amounts of methionic acid in an open vessel at about 40°. In this manner, amyl ether, b. p. 168—172°, can be obtained from commercial amyl alcohol in a 90—95% yield, taking into account the amount of alcohol regained. After fractionation over sodium, this amyl ether has b. p. 59·5—60°/10 mm. or 169·9—170·6°/760 mm., $a_D + 0{\cdot}187°$. The commercial amyl alcohol had $a_D - 1{\cdot}03°$ (compare Guye and Gautier, Abstr., 1895, ii, 149, 195; Marckwald, Abstr., 1904, i, 362). It is found, further, that benzenesulphonic acid and sulphuric acid can be employed in the same manner in the preparation of the higher ethers (compare Norton and Prescott, Abstr., 1885, 496; Mamontoff, *J. Russ. Phys. Chem. Soc.*, 1897, **29**, 230). The method of preparation can be employed only in the case of alcohols and ethers with b. p. above 130—140°, and of alcohols which have not too great a tendency to intramolecular fission of water. G. Y.

Action of Alkalis on Sodium Ethyl Thiosulphate. II. AUGUST GUTMANN (*Ber.*, 1908, **41**, 1650—1655. Compare Abstr., 1907, i, 671).—Sodium ethyl thiosulphate when boiled with an alcoholic solution of potassium hydroxide is decomposed with the formation of sodium potassium sulphite, and not sulphate or thiosulphate. Since analysis shows that 1 mol. of sulphite is produced from 1 mol. of sodium ethyl sulphite, the reaction which takes place may be represented thus: $NaEtS_2O_3 + KOH = NaKSO_3 + EtSOH$. The exact nature of the *substance*, EtSOH, which has not been isolated, is not yet known. It is converted by sodium arsenite in alcoholic sodium hydroxide solution, under pressure, into ethyl mercaptan and sodium arsenate: $EtSOH + Na_3AsO_3 = EtSH + Na_3AsO_4$, and by potassium cyanide and potassium sulphide in aqueous solution into ethyl mercaptan and potassium thiocyanate:

$$EtSOH + KCN + K_2S = EtSH + KCNS + KOH.$$

Similarly, sodium ethyl thiosulphate is decomposed by an alcoholic solution of potassium hydrogen sulphide, yielding potassium sodium sulphite and a *substance*, EtS_2H, thus: $NaEtS_2O_3 + KSH = NaKSO_3 + EtS_2H$. The alcoholic solution of the compound EtS_2H, when treated with sodium arsenite or potassium cyanide, yields ethyl mercaptan and sodium monothioarsenate or potassium thiocyanate, thus:

$$EtS_2H + Na_3AsO_3[or\ KCN] = EtSH + Na_3AsSO_3[or\ KCNS].$$

Attempts will be made to isolate the compound EtS_2H. W. H. G.

Hydrates of the Fatty Acids, according to Measurements of the Viscosity of their Solutions. D. E. Tsakalotos (*Compt. rend.*, 1908, **146**, 1146—1149. Compare this vol., ii, 260; Dunstan, Abstr., 1904, ii, 805).—The viscosities of aqueous solutions of formic, acetic, propionic, and *n*-butyric acids of different strengths have been measured at 20° by the Poiseuille-Ostwald method, the densities of the liquids being determined by means of a Sprengel-Ostwald pyknometer. The viscosity-coefficients (η) were calculated from the formula $\eta = kdt$, where k is the constant of the apparatus, d the density of the solution, and t its time of flow. To determine k, an experiment was made with benzene, the value of η/d being found from Guye and Friderich's table. The results are given in tabular form. Whilst the viscosity of pure formic acid is greater than those of its homologues, the aqueous solutions of the latter are more viscous than those of formic acid. When the viscosities of the solutions are plotted against their concentrations, the curves obtained for acetic, propionic, and *n*-butyric acid exhibit well-defined maxima corresponding with concentrations of equal molecular quantities of acid and water, indicating the existence of the hydrates $CH_3{\cdot}CO_2H,H_2O$, $C_2H_5{\cdot}CO_2H,H_2O$, and $C_3H_7{\cdot}CO_2H,H_2O$. The curve for formic acid, on the contrary, shows a regular decrease in viscosity from pure acid to pure water. *iso*Butyric acid and water form two layers at concentrations between 20% and 50% of acid; the viscosities of the homogeneous solutions are higher than the values calculated by the rule of mixtures. E. H.

Action of Concentrated Sulphuric Acid on Glycerol Esters of Saturated Monobasic Fatty Acids. B. W. van Eldik Thieme (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 855—860).—As is well known, the hydrolysis of esters is a reversible reaction: $R{\cdot}CO_2R' + H_2O \rightleftharpoons R{\cdot}CO_2H + R'{\cdot}OH$; the equilibrium between the reacting molecules is dependent on the temperature, the nature of the medium, and the nature of the ester. The velocity of the hydrolysis, which is low, is accelerated by hydrogen ions, but, so long as the amount of acid added is insufficient to modify markedly the nature of the medium, the equilibrium is unchanged. Hence the saponification of fats by dilute sulphuric acid cannot be carried to completion, but if concentrated sulphuric acid is employed, not only is the nature of the medium altered, but the reaction now takes place according to the equation: $R{\cdot}CO_2R' + H_2SO_4 \rightleftharpoons R{\cdot}CO_2H + R'{\cdot}O{\cdot}SO_3H$, and the equilibrium may be shifted completely to the right if the acid is anhydrous, if an excess of the acid is added to the dry fat, and if the temperature is maintained within certain limits. The following experiments show the influence of these three conditions on the saponification. Contrary to Bünte's statement (Abstr., 1895, ii, 95), butter-fat cannot be saponified completely by 93·5% sulphuric acid at 30—32°. It is found that at that temperature 81% of the butter-fat is hydrolysed by 93·5% sulphuric acid, 89·7% by 98·5% acid, and 92·2% by 100% acid. At 18°, 86·6% of trilaurin is saponified by 6·5 mols. of 100% sulphuric acid, 95·5% by 26 mols. of the same acid, and 100% by 52 mols. of the acid. If the mixture of sulphuric acid and completely saponified trilaurin is heated for one hour at 60°, 12·9% of trilaurin is again formed (compare Grün and Schacht, Abstr., 1907, i, 462). Lauric and sulphuric acids must form a molecular compound, as dry benzene extracts both acids from a mixture of trilaurin and 100% sulphuric acid (compare Hoogewerff and van Dorp, Abstr., 1899, i, 672; Meiger, *Monatsh.*, 1903, **24**, 840). When heated with 52 mols. of 94·6% sulphuric acid, trilaurin yields 80% of lauric acid and 20% of mixed glycerides. It is considered that the mono- and di-laurins in this mixture are formed by the action of water on the compounds $C_{11}H_{23}\cdot CO\cdot O\cdot C_3H_5(O\cdot SO_3H)_2$ and $C_3H_5(O\cdot CO\cdot C_{11}H_{23})_2\cdot O\cdot SO_3H$.

Grün and Schacht (*loc. cit.*) state that the action of sulphuric acid on glycerol leads to the formation of only glycerolmono- and glyceroldi-sulphuric acids. Experiments are now quoted showing that, on the contrary, the product of the action of 98·3% sulphuric acid is chiefly the tri- and di-sulphuric acids, only small amounts of glycerolmonosulphuric acid being formed, but that if the mixture is diluted with water the trisulphuric acid undergoes partial hydrolysis to the di- and mono-sulphuric acids (compare Claësson, Abstr., 1879, 1033).

G. Y.

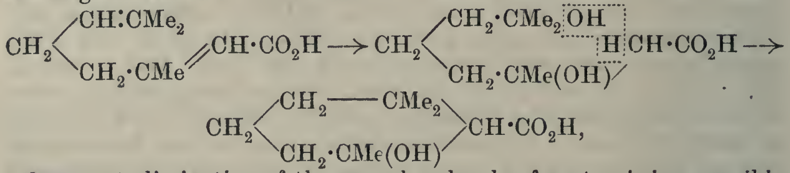
Theory of the Saponification of the Glycerides. Rudolf Wegscheider (*Monatsh.*, 1908, **29**, 233—234).—Corrections of a few errors in a previous paper (this vol., ii, 165).

W. H. G.

Theory of Saponification. IV. Richard Fanto and Milan J. Stritar (*Monatsh.*, 1908, **29**, 299—316).—A continuation of the authors' investigation on the hydrolysis of fats (compare Abstr., 1907, i, 464).—The hydrolysis of tallow, beef-fat, tripalmitin, and olive-oil by solutions of potassium hydroxide in absolute, 95%, and 90% alcohol, sometimes in the presence of benzene, has been studied in the manner previously described (Abstr., 1904, i, 843; 1907, i, 277). The mixture of fats which is obtained on treating tripalmitin with an insufficient quantity of potassium hydroxide has also been investigated. The results obtained may be summarised as follows: (1) The hydrolysis of fats by aqueous potassium hydroxide (heterogeneous system) takes place directly. (2) The transformation of fats into ethyl esters under the influence of alcoholic potassium hydroxide solutions ("alcoholysis") in homogeneous systems proceeds throughout in separate stages. The same reaction also takes place in apparently heterogeneous systems; a perfect heterogeneous system cannot, however, be obtained with the constituents employed in studying this change, owing to the miscibility of the various substances produced by the esters. (3) The higher the percentage of water in the alcoholic potassium hydroxide solutions the closer does the course of the reaction approach to the direct hydrolysis of the true heterogeneous system.

W. H. G.

Mechanism of the Ring Formations in the Geranic Series; Synthesis and Structure of Dihydromyrcene. MARC TIFFENEAU (*Compt. rend.*, 1908, **146**, 1153—1155).—Tiemann (Abstr., 1898, i, 374) has explained the formation of isomeric cyclic compounds from derivatives of the geranic series by successive fixation and elimination of two molecules of water, although Barbier and Bouveault had shown (Abstr., 1897, i, 537) that, strictly, a single molecule was sufficient for the ring formation subsequent elimination of the second molecule of water being possible in two ways, thus giving rise to isomeric derivatives. To test the validity of this hypothesis, the author has studied the isomeric change of geranic compounds, in which the hydrogen atoms (one or both) combined with the carbon atom joined to the carboxyl group are substituted by alkyl groups.



When methylheptenone is condensed in the presence of zinc or magnesium with ethyl α-bromopropionate or ethyl or amyl α-chloropropionate, the ethyl or amyl ester of *β-hydroxy-α-methyl-αβ-dihydrogeranic acid* [*β-hydroxy-αβζ-trimethyl-Δ^ε-octenoic acid*],

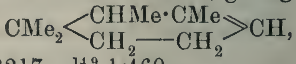
$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CHMe\cdot CO_2H$,

is formed. The *ethyl* ester has b. p. 145—146°/15 mm., D^0 0·9694; the *amyl* ester, 175—185°/14 mm. (decomp.), D^0 0·953. Each of these esters is transformed by acetyl chloride into the corresponding ester of α-methylgeranic acid. *Ethyl α-methylgeranate*,

$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe\colon CMe\cdot CO_2Et$,

has b. p. 239—240°, D^0 0·9259; the *amyl* ester has b. p. 275—277°, D^0 0·9134. Both esters on saponification give *α-methylgeranic acid*, b. p. 156—158°/13 mm., D^0 0·964, which when distilled slowly at ordinary pressure loses carbon dioxide and forms Semmler's dihydromyrcene, $CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe\colon CHMe$ (Abstr., 1901, i, 732), thus showing that the dehydration of the β-hydroxy-α-methyl-αβ-dihydrogeranic acid is effected at the expense of the hydrogen combined with the neighbouring tertiary carbon atom.

α-Methylgeranic acid, but not its amyl ester, is transformed by sulphuric acid into a cyclic *acid*, b. p. 155—158°/11 mm., D^0 1·0071, which on distillation at ordinary pressure loses carbon dioxide, giving Semmler's *cyclo*dihydromyrcene (*loc. cit.*), $CMe_2<\genfrac{}{}{0pt}{}{CHMe\cdot CMe}{CH_2—CH_2}>CH$, b. p. 168—170°/70 mm., D^0 0·8325, $D^{14\cdot9}$ 0·8217, $n_D^{14\cdot9}$ 1·460.



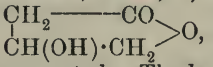
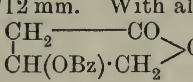
Condensation of methylheptenone with ethyl bromo*iso*butyrate gives *ethyl β-hydroxy-αα-dimethyl-αβ-dihydrogeranate* [*ethyl β-hydroxy-ααβζ-tetramethyl-Δ^ε-octenoate*],

$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CMe_2\cdot CO_2Et$,

b. p. 160—163°/14 mm., D^0 0·9644, which on dehydration by acetyl chloride gives *ethyl αα-dimethylgeranate*,

$CMe_2\colon CH\cdot CH_2\cdot CH\colon CMe\cdot CMe_2\cdot CO_2Et$,

b. p. 248—251°, D^0 0·9208, n_D 1·4609. The corresponding *acid* has b. p. 166—168°/15 mm. The ester does not undergo ring formation when treated with sulphuric acid. E. H.

The Lactone of βγ-Dihydroxybutyric Acid. P. Carré (*Compt. rend.*, 1908, **146**, 1282—1284. Compare Wagner, Abstr., 1894, i, 563).—When βγ-dihydroxybutyric acid is distilled in a vacuum and the distillate fractionated, there are obtained at 92—93°/12 mm. the lactone of hydroxycrotonic acid (Lespieau, Abstr., 1904, i, 471) and the *lactone* of *βγ-dihydroxybutyric acid*,  $\left.\begin{array}{l}CH_2\text{———}CO\\ CH(OH)\cdot CH_2\end{array}\right>O$, b. p. 174—175°/12 mm. With alkalis, the acid is regenerated. The *benzoyl* derivative,  $\left.\begin{array}{l}CH_2\text{———}CO\\ CH(OBz)\cdot CH_2\end{array}\right>O$, has m. p. 101°. J. C. C.

Condensation of Aldol and Crotonaldehyde with Malonic Acid. Adolf Riedel (*Annalen*, 1908, **361**, 89—95).—When heated with pyridine in a reflux apparatus, aldol and malonic acid condense, forming sorbic acid and anhydrohydroxydihydrosorbic acid. It is considered that the first product of the reaction is probably βδ-dihydroxybutylmalonic acid, $OH\cdot CHMe\cdot CH_2\cdot CH(OH)\cdot CH(CO_2H)_2$, which loses carbon dioxide and water, forming β-hydroxydihydrosorbic acid, $CHMe{:}CH\cdot CH(OH)\cdot CH_2\cdot CO_2H$, two molecules of this then forming the anhydro-acid.

Anhydrohydroxydihydrosorbic acid, $C_{12}H_{18}O_5$, is obtained as a viscid, yellow oil, which loses water, changing into sorbic acid, slowly at the ordinary temperature, but more rapidly when boiled with concentrated hydrochloric acid or when distilled in a vacuum. The *silver*, $C_{12}H_{16}O_5Ag_2$, *barium*, $C_{12}H_{16}O_5Ba,4H_2O$, and *copper*, $C_{36}H_{50}O_{15}Cu_2$, salts decompose when heated, forming the corresponding sorbates.

When heated together in quinoline, aldol and malonic acid yield an *acid*, $C_{12}H_{16}O_4,H_2O$, which is obtained as a resinous, reddish-yellow oil, and is considered to be a polymeride of sorbic acid. The *silver*, $(C_{12}H_{14}O_4Ag_2)_x$, and *copper*, $(C_{12}H_{14}O_4Cu)_x$, salts are described.

The action of crotonaldehyde on malonic acid in pyridine solution at the ordinary temperature leads to the formation of sorbic acid and small amounts of *crotonylidenemalonic acid*, $CHMe{:}CH\cdot CH{:}C(CO_2H)_2$, which separates from a mixture of benzene and light petroleum in yellow, granular crystals, m. p. 76°, and on further heating loses carbon dioxide, forming sorbic acid. G. Y.

The System Chloral–Water. C. van Rossem (*Zeitsch. physikal. Chem.*, 1908, **62**, 681—712. Compare this vol., ii, 361).—The freezing points and boiling points of mixtures of chloral and water in various proportions have been determined. The pure chloral used had m. p. −57·5° and b. p. 97°/740 mm.

The form of the freezing-point curve indicates the existence of three compounds of chloral and water containing these components in the molecular proportions 2:1, 1:1, and 1:7. The first of these is formed very slowly from the components, and undergoes a slow dissociation when fused. Its natural freezing point is about 49°, but the crystals may be heated rapidly to 80° without melting. The ordinary monohydrate, which occurs in two pseudo-symmetric modifications (compare Pope, Trans., 1899, 455), also undergoes a slow dissociation when fused. Its natural freezing point is 47·4°, and the highest melting point observed was 54°. The heptahydrate is rapidly formed from the components, and has a constant melting point of −1·4°; in this case there is no process of slow dissociation in the liquid phase.

When mixtures of chloral and water are boiled under a pressure of 740 mm., the composition of the vapour is for all concentrations only very slightly different from that of the liquid. When the boiling temperature is plotted against composition, a curve is obtained with a minimum and two points of inflexion. The boiling point of chloral hydrate is lower than that of either component, but does not coincide with the minimum on the boiling-point curve.

At the ordinary temperature, mixtures of chloral and water form two layers to begin with, but after a time become homogeneous, a considerable amount of heat being developed. At high temperatures (170° and above), homogeneous mixtures of chloral and water separate into two layers, the temperature of separation varying with the composition. The lowest temperature of separation observed was in the case of a mixture containing 60 molecular per cent. of chloral.

J. C. P.

Preparation of Methyl α-Chloropropyl Ketone. Georg Korschun (*Bull. Soc. chim.*, 1908, [iv], **3**, 595—596. Compare Vladesco, Abstr., 1891, 1183).—This chloro-ketone was prepared by a method already used for methyl α-chloroethyl ketone (Abstr., 1905, i, 373), namely, the passage of a mixture of chlorine and carbon dioxide through methyl propyl ketone, cooled in a freezing mixture, and contained in a glass vessel connected to a second vessel containing distilled water. The passage of the two gases is continued until the increase in weight of the two vessels and their contents is equal to about 80% of the weight of ketone taken. The chloro-ketone is then isolated by fractional distillation, the portion having b. p. 63°/95 mm. being collected. The yield is 56·4 per cent.

T. A. H

Acetylacetone Compounds of Metals of Group II. Sebastian M. Tanatar and E. Kurovski (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 580—584).—In continuation of their work on the atomic weight of glucinum (Abstr., 1907, i, 888; ii, 261), the authors have prepared the acetylacetone compounds of the metals of the second group in order to compare them with the corresponding glucinum compound. The only one of these compounds resembling that of glucinum is the zinc derivative. But whilst zinc and also cadmium readily form basic acetylacetone derivatives, no basic glucinum compound is formed even on boiling a solution of the normal acetylacetone compound with glucinum carbonate and oxide.

Magnesium acetylacetone, $Mg(CHAc_2)_2$, forms long, white crystals and exhibits normal ebullioscopic behaviour in alcohol.

Calcium acetylacetone, $Ca(CHAc_2)_2,2H_2O$, forms white, acicular crystals.

Zinc acetylacetone, $Zn(CHAc_2)_2$, forms yellow crystals, m. p. 130°, can be distilled at a pressure of 350 mm., and has the normal molecular weight in boiling alcohol.

Strontium acetylacetone, $Sr(CHAc_2)_2,2H_2O$, in insoluble in any of the ordinary solvents.

Basic cadmium acetylacetone, $Cd(CHAc_2)_2,CdO$, is amorphous; the normal salt could not be prepared.

Barium acetylacetone, $Ba(CHAc_2)_2,2H_2O$, crystallises in plates.

Mercuric acetylacetone, $Hg(CHAc_2)_2$, forms white crystals.

T. H. P.

Application of Barfoed's Reagent to Show the Hydrolysis of Disaccharides by Enzymes. HERBERT E. ROAF (*Bio.-Chem. J.*, 1908, **3**, 182—184).—The presence of lactase and maltase may be determined readily by the use of Barfoed's reagent, which when used with certain precautions is not reduced by disaccharides, but is reduced by the monosaccharides into which they are decomposed.

W. D. H.

The Properties of Starch in Relation to its Colloidal Condition. EUGÈNE FOUARD (*Compt. rend.*, 1908, **146**, 978—981. Compare this vol., i, 138).—The physical properties of true "soluble starch," filtered through a membrane of collodion, have been further investigated.

The freezing-point depression is nil, so that soluble starch has no osmotic pressure. If the freezing-point depression be taken as less than 0·001°, the molecular weight must be more than 15,000, equivalent to a cluster of 45 molecules of maltose. This, however, is not the initial condition of the molecules, since the act of freezing brings about a slight opalescence of the solution.

Ultramicroscopic examination shows that the particles are much smaller than those in colloidal starch solution, soluble starch being, in fact, indistinguishable from many other true solutions.

Soluble starch may have $[\alpha]_D$ 183°15′ to 191°50′, according to the texture of the collodion filter employed. The greater the proportion of starch which passes through the filter the higher the specific rotatory power. The various collodion filters may be compared with a set of sieves of different mesh which sort out molecular aggregates of various sizes.

When a solution which passed entirely through the filter was evaporated down in a vacuum at 15° or in the drying-oven at 60°, it would no longer pass through entirely. Dilution of this solution increased the amount which passed from 71·1% to 91·0% of the total starch present. Thus partial evaporation and subsequent dilution served to destroy the condition of perfect solubility of the starch. The author concludes that water itself is an essential factor in modifying the molecular aggregation of pure starch. The action is a reversible hydrolysis in accordance with the law of mass action. Soluble starch molecules are not necessarily already formed in natural starch, but are more probably formed by the hydrolysing action of water on it. When a true solution of starch is allowed to age, it sets to a compact magma. This change is reversible, is accelerated by acids or low temperature, and retarded by alkalis or heat.

When a starch solution is converted into the granular condition, the conductivity increases from about $73 \cdot 4 \times 10^{-6}$ to a constant value of $226 \cdot 7 \times 10^{-6}$. Since the solutions contain a very slight trace of a weak acid, perhaps an acid phosphate (compare Abstr., 1907, i, 391), the increase in conductivity is ascribed to the liberation of the molecules of this electrolyte which remain combined with the soluble starch until the latter is polymerised. When the above-mentioned maximum conductivity is reached, no further granulation occurs, although only a small fraction of the total starch has been coagulated.

A very important relationship must subsist between the organic starch molecule and its saline environment. R. J. C.

Highly Nitrated Cellulose, Hydrocellulose, and Oxycellulose. Ernst Berl and R. Klaye (*Chem. Zentr.*, 1908, i, 1381; from *Zeitsch. Schiess. Sprengstoffwesen*, 1907, 2, 381—387. Compare Abstr., 1907, i, 390).—With the object of ascertaining whether highly nitrated cellulose (13·5% *N*) is true cellulose nitrate, oxycellulose nitrate, hydrocellulose nitrate, or a mixture of these substances, nitration experiments have been carried out with cellulose, hydrocellulose, and oxycellulose under exactly similar conditions. The substances used were cellulose, hydrocellulose, hydralcellulose, $KMnO_4$-cellulose, Br-oxycellulose, HNO_3-oxycellulose, $KClO_3$-oxycellulose, bleaching powder-oxycellulose, and a new *oxycellulose* prepared by the authors by means of calcium permanganate, all of which, besides being freed from fat, were analysed, microscopically examined, and tested with methylene-blue, Fehling's solution, &c. The results show that the product of nitrating pure cellulose at the ordinary temperature is pure cellulose ester; hydrocellulose and oxycellulose, under the same conditions, are not capable of being so highly nitrated as pure cellulose. The solubility of the nitrate from hydro- or oxy-cellulose in a mixture of ether and alcohol is the same as that of the product from pure cellulose which has the same nitrogen content. Hydro- and oxy-cellulose nitrate exhibit a greater attraction for methylene-blue than does the HNO_3-ester of pure cellulose of identical nitrogen content. Cellulose, hydro- and oxy-cellulose have a greater attraction for methylene-blue than their nitric acid-esters. The viscosity of acetone solutions of nitrates of pure cellulose is considerably greater than that of similar solutions of the nitrates of hydro- and oxy-cellulose having the same nitrogen content and prepared at the same temperature. J. V. E.

Gradual Nitration of Cellulose and Denitrification of Cellulose Nitrate by means of Acid Mixtures. Ernst Berl and R. Klaye (*Chem. Zentr.*, 1908, i, 1381—1382; from *Zeitsch. Schiess. Sprengstoffwesen*, 1907, 2, 403—406).—It is shown that a cellulose nitrate (13·86% N), prepared by means of nitrogen pentoxide, is stable when treated with hot water, so the cause of the esterification of cellulose by means of nitric and sulphuric acids not taking place to the theoretical extent (14·14% N) is not due to the instability of the product when containing more than 13·5% N. Rather is it to be ascribed to the sulphuric acid, which, besides favouring the nitration by removing water, has a tendency to hydrolyse the nitric acid-ester, as also have the H-ions of the nitric acid. Equilibrium is established between the ester formed and the acid, and it follows that for every acid mixture a definite cellulose nitrate should be produced. The validity of this explanation is shown by the examination of the product obtained from treating pure cellulose and three different cellulose nitrates with acid mixtures of various strengths, the time of action and the temperature being also varied. J. V. E.

Cellulose Nitrates and Cellulose Acetonitrates. Ernst Berl and Watson Smith, jun. (*Ber.*, 1908, **41**, 1837—1844).—When treated with nitric acid and an excess of acetic anhydride, cellulose yields highly nitrated products; acetylation does not occur. Similar products are formed when Pictet and Khotinsky's acetyl nitrate (Abstr., 1907, i, 175) is used. When, however, sulphuric acid is present, acetyl nitrates of cellulose are formed, probably owing to the sulphuric acid hydrolysing several of the nitrate groups and subsequent acetylation. The percentage of nitrogen in these mixed esters tends to increase as the proportion of acetic anhydride to the acid mixture is decreased. The nitrates obtained in the absence of sulphuric acid appear to be less soluble in concentrated sulphuric acid than the ordinary nitrates.

When the proportion of acetic anhydride is small, nitrates are not formed to any appreciable extent. J. J. S.

A Lævorotatory Substance Found in Altered Beetroot. Julius Weisberg (*Bull. Soc. chim.*, 1908, [iv], **3**, 601—604; *Bull. Assoc. chim. Sucr. Dist.*, 1908, **25**, 946—949*).—Examination of juice expressed from beetroot, which had become "frosted" and partly rotten, showed that it contains a lævorotatory substance, which is precipitated by lead subacetate solution and by milk of lime, and which on boiling with dilute mineral acids decomposes, forming dextrorotatory products (arabinose and dextrose?) which reduce Fehling's solution. The substance appears therefore to differ from Fremy's parapectic acid only in being lævorotatory in place of dextrorotatory, and it is proposed to call it *l*-parapectic acid. There is reason to believe that it is formed from the dextrorotatory pectous matter originally present in the roots. T. A. H.

Double Phosphate of Magnesium and Methylamine. Maurice François (*Compt. rend.*, 1908, **146**, 1284—1287).—The author has investigated Quantin's method (Abstr., 1893, ii, 104) of separating ammonia from the methylamines, and finds that, contrary to Quantin's statement, monomethylamine is precipitated by magnesium phosphate, giving *magnesium methylamine phosphate*,

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* and *Zeitsch. Ver. deut. Zuckerind.*, 1908, 505—508.

$Mg(NH_3Me)PO_4,6H_2O$. This is even exclusively formed when equal molecular quantities of ammonia, monomethylamine, and magnesium phosphate are mixed. The latter reagent does not precipitate solutions of di- or tri-methylamine. The conclusion is drawn, therefore, that Quantin's method cannot be applied to the separation of ammonia and monomethylamine, but only to the separation of mixtures of di- and tri-methylamine and ammonia. J. C. C.

Stereochemistry of Chromium. V. Stereoisomeric Aquo- and Hydroxy-salts. Paul Pfeiffer [with R. Prade and R. Stern] (*Zeitsch. anorg. Chem.*, 1908, **58**, 228—256. Compare Abstr., 1907, i, 895; this vol., i, 79).—The preparation and properties of certain stereoisomeric aquo- and hydroxy-salts of chromium are described, including two new examples of structural isomerism.

cis-Dibisaquodiethylenediaminechromium bromide,

$$[En_2Cr(O_2H_4)_2]Br_3,$$

has already been described (*loc. cit.*). The corresponding *chloride*, $[En_2Cr(O_2H_4)_2]Cl_3$, prepared by the action of hydrochloric acid on *cis*-hydroxyaquodiethylenediaminechromium dithionate,

$$[En_2Cr(OH_2)OH]S_2O_6,$$

forms lustrous, orange-red plates. Both salts are considerably hydrolysed in aqueous solution, and from these, by the action of pyridine, the basic salts, $[En_2Cr(O_2H_4)OH]X_2$ (X = Cl or Br), are obtained in claret-red crystals, soluble with neutral reaction in water. By the action of mineral acids on these salts, the dibisaquo-salts are regenerated, as represented by the equation $[En_2Cr(O_2H_4)_2X_3 \rightleftharpoons [En_2Cr(O_2H_4)OH]X_2 + HX + H_2O$. By the action of potassium iodide and dithionate respectively on the hydroxy-salts, the corresponding *iodide*, $[En_2Cr(O_2H_4)OH]I_2$, lustrous, claret-red, compact crystals, and *dithionate*, $[En_2Cr(OH_2)OH]S_2O_6$, small, claret-red needles, have been prepared; the latter contains a molecule of water less than the other salts.

By interaction of the *cis*-dibisaquo-bromide, $[En_2Cr(O_2H_4)_2]Br_3$, and potassium chromium thiocyanate, $K_3Cr(SCN)_6$, in dilute acetic acid solution, the *compound*, $[En_2Cr(O_2H_4)_2][Cr(SCN)_6],H_2O$, is obtained as a red powder. From the same bromide and blue potassium chromium oxalate, $K_3Cr(C_2O_4)_3,3H_2O$, the analogous *compound*,

$$[En_2Cr(O_2H_4)_2][Cr(C_2O_4)_3],7H_2O,$$

is obtained in lustrous, violet-brown leaflets. A compound isomeric with the last-mentioned, of the formula

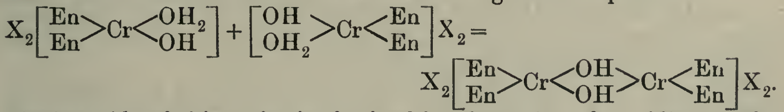
$$[En_2Cr(C_2O_4)][Cr(OH_2)_2(C_2O_4)_2],2H_2O,$$

is obtained in small, lustrous, reddish-yellow crystals by interaction of the oxalato-chloride, $[En_2CrC_2O_4]Cl$, and red potassium chromium oxalate, $[Cr(OH_2)_2(C_2O_4)_2]K,4H_2O$, and subsequent addition of alcohol.

The *trans*-salts are prepared by methods analogous to those just described. The green *trans*-compound, $[En_2CrBr_2]Br$, is considerably hydrolysed in aqueous solution, and on adding potassium bromide and pyridine the basic salt, trans-*hydroxyaquodiethylenediaminechromium bromide*, $[En_2Cr(OH_2)OH]Br_2$, is obtained as lustrous, flesh-coloured leaflets. From the bromide by double decomposition, the corresponding *iodide* and *dithionate* have been prepared; both form flesh-coloured crystals, and, like the bromide, dissolve in water with neutral reaction. By treating the bromide with hydrobromic acid (compare *cis*-series above), *trans*-dibisaquodiethylenediaminechromium bromide, $[En_2Cr(O_2H_4)_2]Br_3$, is obtained in lustrous, prismatic, orange-brown needles; whether two of the water molecules are outside or inside the nucleus is not yet conclusively settled. On treatment with alcohol, or after keeping over phosphoric oxide for some time, the salt loses $2H_2O$, and trans-*diaquodiethylenediaminechromium bromide*, $[En_2Cr(OH_2)_2]Br_3$, is obtained in orange-brown crystals. The *chloride*, *nitrate*, *thiocyanate*, and *oxalate* corresponding with the last-mentioned salt have also been prepared, but the last three salts have not yet been analysed. These salts are considerably hydrolysed in solution, the chief products being the *hydroxyaquo*-salts, $[En_2Cr(OH_2)OH]X_2$, mentioned above as being obtainable by other methods.

The properties of the corresponding compounds belonging to the *cis*- and *trans*-series are compared in detail. G. S.

Stereochemistry of Chromium. VI. Polynucleal Chromium Salts. PAUL PFEIFFER [with W. VORSTER and RICHARD STERN] (*Zeitsch. anorg. Chem.*, 1908, **58**, 272—296. Compare foregoing abstract).—When *cis*-hydroxyaquodiethylenediaminechromium salts, or the corresponding hydroxybisaquo-salts, are heated, they lose water and form diolchromium salts according to the equation


$$X_2\left[\begin{matrix}En\\En\end{matrix}>Cr<\begin{matrix}OH_2\\OH\end{matrix}\right]+\left[\begin{matrix}OH\\OH_2\end{matrix}>Cr<\begin{matrix}En\\En\end{matrix}\right]X_2=$$
$$X_2\left[\begin{matrix}En\\En\end{matrix}>Cr<\begin{matrix}OH\\OH\end{matrix}>Cr<\begin{matrix}En\\En\end{matrix}\right]X_2.$$

The bromide of this series is obtained by the action of pyridine on the dilute aqueous solution of *cis*-dibisaquodiethylenediaminechromium bromide, the hydroxybisaquo-salt being formed as intermediate product.

Tetraethylenediaminedioldichromium bromide,

$$[En_4Cr_2(OH)_2]Br_4,2\tfrac{1}{2}H_2O,$$

forms lustrous, bluish-violet crystals, soluble with neutral reaction in water; the bromine is precipitated quantitatively by silver nitrate. The salt is decomposed on heating with mineral acids; with concentrated hydrochloric acid the cis-*dichloro-chloride*, $[En_2CrCl_2]Cl,H_2O$, is obtained, and with hydrochloric acid the cis-*bromobisaquo-bromide*,

$$[En_2CrO_2H_4Br]Br_2.$$

By double decomposition of the diolbromide with potassium iodide, the corresponding *iodide*, $[En_4Cr_2(OH)_2]I_4,2\frac{1}{2}H_2O$, is obtained in small, bluish-violet, lustrous needles.

A number of hexaethylenediaminehexoltetrachromium salts, which appear to have the general formula $\{Cr[En_2Cr(OH)_2]_3\}X_6$, have been prepared as follows. Partly dehydrated chrome alum is heated for some time with ethylenediamine monohydrate, and the product is then treated with a little water and filtered; the residue is the crude sulphate of the series in question. When the sulphate is treated with hydrochloric acid in moderate excess, *hexaethylenediaminehexoltetrachromium chloride*, $[En_6Cr_4(OH)_6]Cl_6,6H_2O$, is obtained in small, red needles. From this salt by double decomposition, the corresponding *bromide* and *iodide*, with $4H_2O$, *thiocyanate*, with H_2O, *dithionate*, with $7H_2O$, *nitrate*, with $6H_2O$, and *chromate*, with $5H_2O$, have been obtained; all occur in red needles except the chromate, which forms a brownish-red, apparently amorphous powder. A double salt of the iodide and mercuric iodide, of the formula

$$[En_6Cr(OH)_6]I_6,2HgI_2,8H_2O,$$

has also been obtained as a yellowish-red precipitate. These salts are slightly alkaline in reaction, do not unite with hydrochloric acid like the hydroxy-salts, and on heating with concentrated hydrochloric acid are decomposed with production of the *cis*-dichloro-chloride,

$$[En_2CrCl_2]Cl,H_2O.$$

It is pointed out that these red hexol salts appear to be closely related to the rhodoso-salts of Jörgensen. G. S.

Stereochemistry of Chromium. VII. Mixed Luteo-salts. PAUL PFEIFFER [with TH. GASSMANN and H. PIETSCH] (*Zeitsch. anorg. Chem.*, 1908, 58, 297—316. Compare foregoing abstracts).—As the isomerism persists when the nucleus halogen atoms in the cis- and trans-diacidodiethylenediaminechromium (and cobalt) salts, $[En_2CrX_2]X$, are ionised by displacing them by water molecules (previous abstract, Part V), the question was investigated as to whether the cis-trans-isomerism also persists when a halogen in the nucleus is displaced by an ethylamine or propylamine group. This is found not to be the case, identical simple and mixed luteo-salts being obtained from the *cis*- and *trans*-compounds. The change of configuration takes place with the trans-compounds.

The salts were either prepared directly by heating the respective dichloro-chlorides, $[En_2CrCl_2]Cl$ and $[En_2CoCl_2]Cl$, with ethylenediamine and propylenediamine (Pn) respectively until the product became yellow, and then adding the alkali salt of the appropriate acid, or by double decomposition. *Diethylenediaminepropylenediaminechromium bromide*, $[En_2Cr\ Pn]Br_3,2H_2O$, forms lustrous, yellow needles; the *iodide*, with $2H_2O$, and the thiocyanate, with $\frac{1}{2}H_2O$, also form lustrous, yellow needles. *Diethylenediaminepropylenediaminecobalt bromide* $[En_2Co\ Pn]Br_3,3H_2O$, and the *iodide*, with $3\frac{1}{2}H_2O$, occur in brownish-yellow needles; the *thiocyanate*, with $\frac{1}{2}H_2O$, in small, yellow crystals. The solubility of the cobalt salts in water has been determined.

By interaction of the complex chromium and cobalt bromides just mentioned with potassium chromium oxalate and potassium cobalt oxalate respectively in aqueous solution, the four *compounds*, $[En_2Cr\ Pn][Cr(C_2O_4)_3],4\frac{1}{2}H_2O$, silver-grey leaflets,

$$[En_2Cr\ Pn][Co(C_2O_4)_3],4\frac{1}{2}H_2O,$$

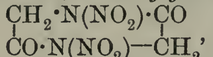
green needles, $[En_2Co\ Pn][Co(C_2O_4)_3],5H_2O$, small green crystals, and $[En_2Co\ Pn][Cr(C_2O_4)_3],4\frac{1}{2}H_2O$, lustrous, silver-grey crystals, have been prepared. The compounds are decomposed into their components by heating with hydrochloric acid. By an analogous method, the four corresponding *cyanides* have been prepared, all of which occur in yellow crystals. G. S.

Distillation of Esters of Amino-acids by means of the Geryk Pump. PHŒBUS A. LEVENE and D. D. VAN SLYKE (*Biochem. Zeitsch.*, 1908, 10, 214).—A sufficiently low pressure for the fractional distillation of esters of amino-acids was obtained by the use of the Geryk pump, and the use of liquid air avoided, the vessel immersed in liquid air being replaced by one filled with cotton wool saturated with sulphuric acid and immersed in a freezing mixture.

W. D. H.

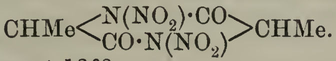
Nitration and Acetylation of Glycine Anhydride and its Methyl Homologues: Alanine Anhydride and α-Amino*iso*butyric Anhydride.

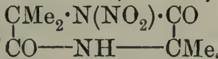
Antoine P. N. Franchimont and **H. Friedmann** (*Rec. trav. chim.*, 1908, **27**, 192—206. Compare Donk, Abstr., 1907, i, 831).—When glycine anhydride is added to a mixture of absolute nitric acid and acetic anhydride, *dinitroglycine anhydride*,



$$\begin{array}{l}\mathrm{CH_2\cdot N(NO_2)\cdot CO}\\ \mathrm{CO\cdot N(NO_2)-CH_2}\end{array},$$

is obtained. This compound separates from ethyl acetate in large, glistening plates, which decompose at 145—146°. When dissolved in alcoholic ammonia, it furnishes nitroaminoacetamide, whilst sodium hydroxide converts it into the sodium salt of nitroaminoacetic acid.

Alanine anhydride dissolves in absolute nitric acid with formation of a *dinitrate*, which on treatment with acetic anhydride yields *dinitroalanine anhydride*,  $\mathrm{CHMe}<\begin{matrix}\mathrm{N(NO_2)\cdot CO}\\ \mathrm{CO\cdot N(NO_2)}\end{matrix}>\mathrm{CHMe}$. This forms colourless needles decomposing at 136°.

*Methyl α-amino*iso*butyrate*, $C_5H_{11}O_2N$, b. p. 136°/749 mm., D_4^{12} 0·9787, was prepared from α-amino*iso*butyric acid; *hydrochloride*, decomp. 183°. When the ester is heated in a closed vessel for thirty-six hours at 230—240°, it forms *α amino*iso*butyric anhydride*, $C_8H_4O_2N_2$, which sublimes without melting. *α-Amino*iso*butyramide*, $C_4H_{10}ON_2$, m. p. 127°, is very soluble in water, alcohol, and chloroform. *α-Nitroamino*iso*butyric anhydride*,  $\begin{array}{l}\mathrm{CMe_2\cdot N(NO_2)\cdot CO}\\ \mathrm{CO{-\!\!-}NH{-\!\!-}CMe_2}\end{array}$, crystallises from hot water in fine colourless needles, m. p. 166° (decomp.). When treated with absolute nitric acid and acetic anhydride, this compound is transformed quantitatively into *dinitro-α-amino*iso*butyric anhydride*, $C_8H_{12}O_6N_4$, rhombohedra, m. p. 108°, insoluble in water, but soluble in alcohol, ether, and benzene.

Diacetylglycine anhydride, $C_8H_{10}O_4N_2$, m. p. 102°, is very soluble in water and alcohol, and is readily prepared by dissolving glycine anhydride in acetic anhydride.

Diacetylalanine anhydride, $C_{10}H_{14}O_4N_2$, m. p. 132°, crystallises from hot water in shining needles. α-Amino*iso*butyric anhydride is not attacked when boiled with acetic anhydride and sodium acetate, or with acetyl chloride.

W. O. W.

Derivatives of Dithiocarbaminoacetic Acid.

H. Körner (*Ber.*, 1908, **41**, 1901—1905).—A study of the action of carbon disulphide on amino-acids.

A solution of *potassium dithiocarbaminoacetate* (*potassium glycine*-N-*dithiocarboxylate*), $CS_2K\cdot NH\cdot CH_2\cdot CO_2K$, is obtained by the action of carbon disulphide on a solution of glycine in aqueous potassium hydroxide. The *acid* is unstable, and on liberation decomposes, forming carbon disulphide. The potassium salt reacts easily with alkyl haloids, forming salts of the type $CS_2R\cdot CH_2\cdot CO_2K$, which on acidification yield stable, crystalline acids, $CS_2R\cdot NH\cdot CH_2\cdot CO_2H$. The S-*ethyl* O-*hydrogen* ester, $CS_2Et\cdot NH\cdot CH_2\cdot CO_2H$, formed by shaking the potassium salt with ethyl bromide, crystallises in white prisms, m. p. 123—124°, and when treated with hydrogen chloride in ethyl-alcoholic solution yields the *ethyl* ester,

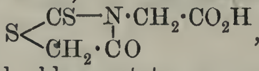
$$CS_2Et\cdot NH\cdot CH_2\cdot CO_2Et,$$

crystallising in white needles, m. p. 72°. The O-*methyl* S-*ethyl* ester, $CS_2Et\cdot NH\cdot CH_2\cdot CO_2Me$, has m. p. 75°.

S-*Carboxymethyl* O-*hydrogen dithiocarbaminoacetate*,

$$CO_2H\cdot CH_2\cdot S\cdot CS\cdot NH\cdot CH_2\cdot CO_2H,$$

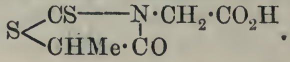
prepared from the potassium salt and potassium chloroacetate, crystallises in white prisms, decomp. 80°, m. p. 120°, and changes when heated at 100°, or more slowly over sulphuric acid at the ordinary temperature, into *rhodaninacetic acid* (4-*keto*-2-*thiothiazolidine*-3-*acetic acid*),



$S<\begin{matrix}CS—N\cdot CH_2\cdot CO_2H\\ CH_2\cdot CO\end{matrix}$

, which is formed also by the action of ethyl chloroacetate on potassium dithiocarbaminoacetate. It crystallises in yellow needles, m. p. 148°, and, when dissolved in hot water, again forms *S*-carboxymethyl *O*-hydrogen dithiocarbaminoacetate. *Ethyl rhodaninacetate*, $C_7H_9O_3NS_2$, crystallises in yellow needles, m. p. 58°. The *methyl* ester is obtained as a yellow oil which rapidly solidifies.

The action of α-bromopropionic acid on potassium dithiocarbaminoacetate leads to the formation of 4-*keto*-2-*thio*-5-*methylthiazolidine*-3-*acetic acid*,



$S<\begin{matrix}CS—N\cdot CH_2\cdot CO_2H\\ CHMe\cdot CO\end{matrix}$.

G. Y.

Hydroxyprolines. Hermann Leuchs and Heinrich Felser (*Ber.*, 1908, **41**, 1726—1735).—The two synthetical hydroxyprolines (Abstr., 1905, i, 545) when reduced with hydriodic acid and red phosphorus at 140—150° yield proline (pyrrolidine-2-carboxylic acid). Both acids combine with phenylcarbimide, yielding *derivatives*,

$$C_{12}H_{14}O_4N_2;$$

that from the α-acid crystallises from water in four-sided plates, m. p. 194—195° (corr., decomp.), and that from the β-acid forms six-sided plates, m. p. 187° (corr.). The phenylcarbimide derivatives readily yield *phenylhydantoins*, $C_{12}H_{12}O_3N_2$, when heated with dilute hydrochloric acid, these melt respectively at 164—165° (corr.) and 156—158° (corr.).

In order to determine whether one of the two artificial hydroxyprolines is the racemic form of the hydroxyproline obtained by hydrolysing gelatin, attempts have been made to racemise the natural product, but without success; the stability of this acid indicates that the hydroxy-group is in the β- or γ-position. Attempts to resolve the artificial acids did not meet with success.

δ-Chloro-α-bromovalerolactone reacts with aqueous methylamine, yielding a mixture of two hydroxyhygric acids. The two are readily separated by means of their copper salts, one of which is insoluble in alcohol.

The *b-γ-hydroxy-*N*-methylproline* (*hydroxyhygric acid*), $C_6H_{11}O_3N$, obtained from this insoluble copper salt is identical with the product obtained by methylating *b*-γ-hydroxyproline. It crystallises from methyl alcohol in irregular polyhedra, m. p. 226—227° (corr.) (decomp.). The isomeric *a*-γ-hydroxy-*N*-methylproline crystallises in needles, m. p. 207—208° (corr.) (decomp.). J. J. S.

α-Amino-*n*-hexoic Acid [Leucine]. H. KUDIELKA (*Monatsh.*, 1908, **29**, 351—358).—The author has prepared leucine by Fischer's method (Abstr., 1900, i, 646) from both natural and synthetical *n*-hexoic acids. Using Kahlbaum's preparations, 100 parts of the latter gave 37 parts of leucine, whilst 100 parts of the former gave only 6 parts. The *copper* salt, pale blue leaflets, *nickel* salt, greenish-blue salt, and *cobalt* salt, red leaflets, are described. The *methylated base* forms an *aurichloride*, $C_9H_{19}O_2N,HAuCl_4$, yellow leaflets, m. p. 142°. The solubilities of *d*- and *l*-leucine and of their copper salts in water are recorded. J. C. C.

sec.-Aminoacetals. CARL PAAL and LEO VAN GEMBER (*Arch. Pharm.*, 1908, **246**, 306—314).—The authors have prepared a number of *sec.*-aminoacetals by the action of primary alkylamines on chloroacetal:

$$2Alk\cdot NH_2 + CH_2Cl\cdot CH(OEt)_2 = Alk\cdot NH\cdot CH_2\cdot CH(OEt)_2 + Alk\cdot NH_2,HCl.$$

Tertiary bases are also formed in this reaction, which, however, were not investigated. The alkylaminoacetals are basic oils with an unpleasant odour, and are soluble in water. n-*Propylaminoacetal*, b. p. 185—192°, forms a *hydrochloride*, white, hygroscopic needles, m. p. 103—105°, a *hydrogen oxalate*, m. p. 175°, a *nitrosoamine*, viscid, yellow oil, and a *phenylthiocarbamide*,

$$NHPh\cdot CS\cdot N(C_3H_7)\cdot CH(OEt)_2,$$

white needles, m. p. 44—47°. *Allylaminoacetal*, b. p. 194—197°, forms a *hydrochloride*, m. p. 110—112°, a *hydrogen oxalate*, m. p. 175°, a *nitrosoamine*, a viscid, brownish-yellow oil, a *benzoyl* derivative,

$$C_3H_5\cdot NBz\cdot CH_2\cdot CH(OEt)_2,$$

viscid, yellow oil, a *phenylcarbamide*, yellow oil, and a *phenylthiocarbamide*, white, stellate needles, m. p. 81—82°. n-*Butylaminoacetal*, b. p. 207—210°, is a colourless, mobile liquid, of which the *hydrogen oxalate*, m. p. 190°, the *nitrosoamine*, brown, viscid oil, the *benzoyl* derivative, yellow, viscous oil, the *phenylcarbamide*, m. p. 50—52°, and the *phenylthiocarbamide*, m. p. 51—54°, were prepared. iso*Amylaminoacetal*, b. p. 215—220°, gives a *hydrochloride*, colourless plates, m. p. 33°, a *hydrogen oxalate*, m. p. 204°, a *nitrosoamine*, yellow oil; a *benzoyl* derivative, viscid oil, and a *phenylthiocarbamide*, m. p. 38—42°. J. C. C.

Properties of the Metallic Dithiocarbamates. MARCEL DELÉPINE (*Compt. rend.*, 1908, **146**, 981—984; *Bull. Soc. chim.*, 1908, [iv], 3, 643—652. Compare Abstr., 1907, i, 594).—The author has prepared well-crystallised specimens representative of various types of dithiocarbamides, namely:

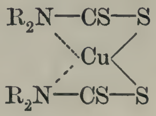
I. $(NH_2{\cdot}CS_2)_2Ni$ and $(NH_2{\cdot}CS_2)_3Co,2C_3H_6O$ (acetone).
II. $NHPr{\cdot}CS_2Na,4H_2O$, $C_4H_9{\cdot}NH{\cdot}CS_2Na,4H_2O$, and $NHPh{\cdot}CS_2Na,3H_2O$.
III. $(C_4H_9{\cdot}NH{\cdot}CS_2)_2Ba,2H_2O$, $NMe_2{\cdot}CS_2Na,2\frac{1}{2}H_2O$, and $N(C_4H_9)_2{\cdot}CS_2Na,4H_2O$.
IV. $NHPr{\cdot}CS_2Cu'$; $(C_4H_9{\cdot}NH{\cdot}CS_2)_2Zn$, and $(NHPh{\cdot}CS_2)_3Co$.
V. $N(C_4H_9)_2{\cdot}CS_2Ag$; $[N(C_4H_9)_2{\cdot}CS_2]_2Pb$; $[N(C_4H_9)_2{\cdot}CS_2]_2Cu$, and $[N(C_4H_9)_2{\cdot}CS_2]_2Ni$.
VI. $(NMe_2{\cdot}CS_2)_3Co,2CHCl_3$; $[N(C_4H_9)_2{\cdot}CS_2]_3Co$, and $[N(C_4H_9)_2{\cdot}CS_2]_3Fe$.

The salts, which are often soluble in ether, chloroform, benzene, and carbon disulphide, have a tendency to crystallise with their solvent. Salts of alkali and alkaline-earth metals, also of zinc, are colourless; those of copper, nickel, cobalt, and iron are intensely and variously coloured, but without regard to the ordinary colours of these metals, in their salts. Ferrous and cobaltous salt could not be obtained, but, on the other hand, cupric salts rapidly and spontaneously change into cuprous salts. The salts $NHPr{\cdot}CS_2Na$ and $NMe_2{\cdot}CS_2Na$ produce twice the theoretical freezing-point depression in aqueous solution.

In benzene or ethylene dibromide, the salts $[NBu_2CS_2]_2Ni$ and $[NBu_2{\cdot}CS_2]_3Co$ $[Bu = C_4H_9]$, as also the ferric salt, give normal freezing-point depressions, showing that they correspond with the type RX_3, and not with the type R_2X_6.

The copper salt, $[NBu_2{\cdot}CS_2]_2Cu$, gives a non-conducting solution in benzene, although the dry compound becomes electrified when pulverised. The absence of conductivity in solutions of these salts in moist organic solvents corresponds with a considerable indifference towards reagents. Thus copper is not precipitated by hydrogen sulphide, or nickel, cobalt, or iron by ammonium sulphide. $NBu_2{\cdot}CSAg$ produces no precipitate even after ten minutes with hydrochloric acid. Lead, however, is easily precipitated from the dithiocarbamates by sulphuric acid or hydroogren sulphide.

The author contends that metallic dithiocarbamates are really internal metallic complexes, and not true salts of the metals. They can be represented as



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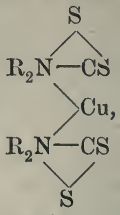


according as Werner's or Blomstrand and Jörgensen's notation is adopted. The alkali metals, which form true salts, can be replaced by copper present as oxide, and the copper dithiocarbamates are also stable in presence of sulphuric acid. Furthermore, several of the compounds are volatile; thus nickel and copper di*iso*butyldithiocarbamates distil unchanged in a vacuum. R. J. C.

Hydrolysis of Aqueous Solutions of Ammonium Thiocyanate in Presence of Metallic Hydroxides. Hermann Grossmann (*Zeitsch. anorg. Chem.*, 1908, 58, 265—271).—The freshly-

precipitated, well-washed hydroxides were boiled with a 10% aqueous solution of ammonium thiocyanate until no further change occurred. In these circumstances, the hydroxides of the alkalis and alkaline earths, including lithium and magnesium, decomposed the ammonium salt completely, the thiocyanates of the respective metals remaining in solution. With hydroxides of less basic character, there are three possible cases: (1) salts with complex cations are formed, for example, $Zn(NH_3)_2(SCN)_2$ and $Cu(NH_3)_2(SCN)_2$; (2) salts with complex anions are formed, for example, $NH_4[Ag(SCN)_2]$ and $(NH_4)_2[Co(SCN)_4],4H_2O$; (3) both complex cations and anions may be formed. As examples of the last class, the compounds $Hg_2ONH_2(SCN)_2$ and

$$(NH_4)_2[Hg(SCN)_4]$$

(Fleischer, 1875), as well as the cadmium compounds, $Cd(NH_3)(SCN)_2$, $Cd(NH_3)_2(SCN)_2$, and $(NH_4)_2Cd(SCN)_4,2H_2O$, are already known, and by slightly modified methods the compounds $Ni(NH_3)_2(SCN)_2$, bluish-green crystals, and $Ni(NH_3)_4(SCN)_2$, dark blue crystals, have been prepared.

Hydroxides of very slight basic character, such as those of glucinum, aluminium, iron (ferric), and chromium, have practically no action on ammonium thiocyanate at boiling temperature. G. S.

[Hexathiocyano-salts of Molybdenum.] Johanna Maas and Julius Sand (*Ber.*, 1908, **41**, 1861).—A correction. It has been found possible to prepare the characteristic yellow zinc salt of the hexathiocyano-series as follows: an excess of ammonium thiocyanate is added to a solution of the green molybdenum trichloride containing hydrochloric acid, and kept at the ordinary temperature for twelve hours, air being excluded; the resulting liquid is then rendered ammoniacal, and finally treated with an ammoniacal solution of zinc chloride.

Since the yellow salts are formed in the absence of air, they must be aquo-salts having the general formula $Mo(SCN)_6(OH_2)R_3$, and not compounds of the type $Mo(SCN)_6(OH)R_3$ as stated previously (this vol., i, 397). W. H. G.

Thiocyanoselenious Acid: New Method for Estimating Selenium. W. I. Iwanoff (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 661—664).—*Thiocyanoselenious acid*, $(HCNS)_2,H_2SeO_3$, is formed by the interaction of a thiocyanate and selenious acid in presence of hydrochloric acid, the reactions being expressed by the equations:

$$NH_4CNS + HCl = HCNS + NH_4Cl \text{ and}$$

$$2HCNS + H_2SeO_3 = (HCNS)_2\cdot H_2SeO_3.$$

It separates as a voluminous precipitate, composed of pyramidal crystals. By heating or by the action of water, alcohol, glycerol, acid, or alkali, it decomposes with precipitation of red selenium. When treated with benzene or carbon disulphide, it dissolves partly, giving a yellow solution, which, on shaking with water, yields a colloidal selenium solution having at first a rose-red, and later a purple, colour. Nitric acid dissolves and oxidises it into selenious and sulphuric acids.

Attempts to prepare an analogous tellurium compound were unsuccessful.

The instability of thiocyanoselenious acid affords a ready means of estimating selenium. To a solution containing from 0·1 to 0·4 gram of selenium, and diluted to about 600 c.c. with water, are added 20—30 c.c. of ammonium or potassium thiocyanate solution, and, after thorough stirring, about 150 c.c. of 25% hydrochloric acid. After being heated on a water-bath for twelve hours, the solution is filtered through a filter previously dried at 105° and weighed, the amorphous selenium on the filter being well washed with hot water, dried at 105°, and weighed. The precipitate often contains a small proportion of sulphur, which may be estimated by oxidising the precipitate in a glass or porcelain beaker with aqua regia, evaporating with hydrochloric acid to expel the nitric acid, dissolving the residue in hydrochloric acid and hot water, filtering, and precipitating with barium chloride. This method gives much better results than washing the precipitate with carbon disulphide, as in some cases part of the selenium is dissolved by this solvent, whilst in others, both sulphur and selenium remain undissolved. T. H. P.

Compounds of Mercuric Cyanide with Alkalis and Nitric Acid. KARL A. HOFMANN and H. WAGNER (*Ber.*, 1908, **41**, 1628—1634. Compare this vol., i, 143).—Mercuric cyanide solution decolorises a solution of phenolphthalein made alkaline with a little sodium hydroxide; this result cannot be due to hydrolysis, as only concentrated solutions of alkali precipitate oxide or basic salt, and from the agreement amongst themselves of the constants, determined by means of the solubility, depression of freezing point, conductivity, and hydrolysis of ethyl acetate, the conclusion is arrived at, that in dilute solutions the complex ion $Hg(CN)_2{\cdot}OH$ is present. Hexagonal crystals having the composition $Hg(CN)_2,KOH,1\frac{1}{2}H_2O$ have been obtained from a solution of 13 grams of mercuric cyanide, 40 grams of potassium hydroxide, and 60 c.c. of water. An aqueous solution of this salt gives crystals of mercuric cyanide on concentration. Oxidising agents, such as hydrogen peroxide, precipitate mercury, and the aqueous solution gives silver cyanide with silver nitrate, mercury acetylide with acetylene, and cyanate with permanganate, showing that this solution is much more reactive than mercuric cyanide solution. The corresponding *sodium* compound, $Hg(CN)_2,NaOH,1\frac{1}{2}H_2O$, forms long prisms, which in a vacuum over phosphoric oxide lose $\frac{1}{2}$ mol. of water. When the operations are carried out in alcoholic instead of aqueous solution, analogous alcohol compounds are obtained. The *sodium* compound,

$$Hg(CN)_2,NaOH,2MeOH,$$

forms hexagonal, doubling refracting prisms, which lose 1 mol. of methyl alcohol in a vacuum over phosphoric oxide; the *potassium* compound is similar, and the *sodium methoxide* derivative,

$$Hg(CN)_2,NaOMe,MeOH,$$

forms rectangular prisms and is stable in a vacuum, but decompose in the light.

A hot solution of mercuric cyanide and 68% nitric acid deposits on cooling the *compound*, $Hg(CN)_2,HNO_3$, which crystallises in needles. It is explosive, and the strongly acid aqueous solution does not give precipitates with either ammonia or alkali, a distinction from the double salt, $Hg(CN)_2,AgNO_3$. W. R.

Constitution of Certain Mercuric Salts with Complex Cations. VINCENZO BORELLI (*Gazzetta*, 1908, 38, i, 361—426).—The author has studied the reactions, cryoscopic behaviour, electrical conductivity, and transport numbers of the complex salts which mercuric cyanide forms with the strongly dissociated mercuric perchlorate and nitrate, and with the feebly dissociated mercuric chloride and acetate. The results indicate that all these complex salts are constitutionally analogous, and all contain the same cation, $HgCN^{\cdot}$. They are hence to be regarded as salts of "cyanomercury" having the constitutions $HgCN\cdot ClO_4$, $HgCN\cdot NO_3$, $HgCN\cdot Cl$, and $HgCN\cdot OAc$, since they all dissociate according to the scheme $(HgCN)A \rightleftharpoons HgCN^{\cdot} + A'$. The complex cyanomercury ion, $HgCN^{\cdot}$, is very stable in all these compounds, and its dissociation according to the equation $HgCN^{\cdot} \rightleftharpoons Hg^{\cdot\cdot} + CN'$ is extremely small in amount. Further, a study of mercuric oxycyanide indicates that its properties are expressed, not by the formula $Hg(CN)_2,HgO$, but by $O(HgCN)_2$, so that it is really cyanomercury oxide, which yields the corresponding hydroxide when dissolved in water. In concentrated, but not in dilute, aqueous solutions, cyanomercury perchlorate, nitrate, and chloride give a precipitate of mercuric oxide on the addition of sodium hydroxide solution, whilst cyanomercury acetate gives a precipitate of cyanomercury oxide under similar conditions. Solutions which are not precipitated by sodium hydroxide give a precipitate with ammonia solution, whilst still more dilute solutions are precipitated only by hydrogen sulphide. With silver nitrate, solutions of the perchlorate, nitrate, or acetate give no precipitate, whilst the chloride gives a precipitate consisting entirely of silver chloride; the concentration of the cyanogen ions is, hence, very small in all cases.

Cyanomercury perchlorate, $(HgCN)ClO_4$, obtained by evaporating a concentrated aqueous solution of mercuric perchlorate (1 mol.) and mercuric cyanide (1 mol.) in a vacuum over sulphuric acid at the ordinary temperature, forms white, acicular prisms, soluble in water or alcohol. In solution it undergoes gradual reduction, with partial formation of mercurous salt. Cryoscopic determinations show that it is dissociated to the extent of 0·80, 0·83, and 0·97 in solutions containing 1, 0·5, and 0·2 mol. respectively per litre. The conductivity in aqueous solution increases considerably with the dilution ($\Lambda_{1024} = 349{\cdot}9$; $\Lambda_{32} = 174{\cdot}4$), the dissociation being of the same order of magnitude as that occurring in solutions of mercuric perchlorate ($\Lambda_{1024} = 296{\cdot}9$; $\Lambda_{32} = 126{\cdot}9$). The transport number of the cation $HgCN^{\cdot}$ with respect to the anion ClO_4' in solutions of medium concentration (0·2 mol. per litre) and at about 20° is about 0·338.

Cyanomercury nitrate, $(HgCN)NO_3$, chloride, $(HgCN)Cl$, and acetate, $(HgCN)C_2H_3O_2$ (compare Prussia, Abstr., 1899, i, 318), exhibit behaviour in general similar to that of the perchlorate. The transport number of the cation $HgCN^{\cdot}$ with respect to the anion NO_3' in solutions of medium concentration at the ordinary temperature is about 0·323. Examination of the products of electrolysis of the chloride in aqueous solution shows that the ion $(HgCN)^{\cdot}$ may give rise to two other ions, namely, the cyanic ion, $(CNO)'$, at the anode and the cyanogen ion, $(CN)'$, at the cathode; the former of these is probably formed by the addition of an atom of oxygen to the cyanogen ions existing in small quantity near the electrode, and the latter by the dissociation of the cyanomercury ion.

That cyanomercury oxide (compare Richard, *J. Pharm. Chim.*, 1903, **18**, 553) forms the corresponding hydroxide, (HgCN)OH, in solution is shown by cryoscopic and ebullioscopic measurements. The solution has a conductivity of the same order of magnitude as that of mercuric cyanide, so that the compound is dissociated to only a slight extent.

T. H. P.

Experiments to Obtain Aliphatic Substituted Oxytriazines and Oxydihydrotriazines. HEINRICH BILTZ [With P. HORRMANN] (*Ber.*, 1908, **41**, 1880—1886).—An account of fruitless attempts to prepare oxytriazines and oxydihydrotriazines of the aliphatic series by methods employed with success in preparing similar aromatic compounds (compare Biltz, Abstr., 1905, i, 491, 673). The work of Diels Abstr., 1902, i, 205; 1903, i, 862), carried out with the same object, has been confirmed.

Diacetyl monosemicarbazone dissolves in aqueous sodium hydroxide without forming an oxytriazine derivative. The *sodium* salt, $C_5H_8O_2N_3Na$, crystallises in nodular aggregates. A mixture of diacetyldioxime and dimethylacetyleneurein (compare Franchimont and Klobbie, Abstr., 1889, 125) is obtained by treating an alcoholic solution of carbamide and diacetyloxime with a few drops of concentrated sulphuric acid.

Diacetyloximesemicarbazone, $C_5H_{10}O_2N_4$, prepared by treating diacetyl oxime with semicarbazide hydrochloride and sodium acetate, has m. p. 247° (decomp.); with a short thermometer, m. p. 259—260° (decomp.); the *acetate* crystallises in aggregates of needles, m. p. 216°.

Dimethylketolsemicarbazone, $OH\cdot CHMe\cdot CMe:N\cdot NH\cdot CO\cdot NH_2$, obtained by acting on dimethylketol with semicarbazide hydrochloride and sodium acetate, has m. p. 194—195° (short thermometer). The solution in concentrated sulphuric acid when carefully diluted yields a substance, m. p. about 270° (decomp.), which is probably diacetyldisemicarbazone. Dimethylketolsemicarbazone decomposes at 200°, yielidng a yellow, vitreous mass.

W. H. G.

Action of Alkalis on Mono- and Di-methylarsonic Acids and their Iodo-derivatives. VICTOR AUGER (*Compt. rend.*, 1908, **146**, 1280—1282).—When sodium methylarsonate is heated with excess of sodium hydroxide at 250—280°, it is decomposed according to the equation: $CH_3\cdot AsO(ONa)_2 + NaOH = CH_4 + AsO(ONa)_3$.

Sodium cacodylate undergoes a similar decomposition, the first stage taking place at 180° as follows:

$$(CH_3)_2AsO(ONa) + NaOH = CH_4 + CH_3\cdot AsO(ONa)_2,$$

the sodium methylarsonate then being decomposed at 260° according to the preceding equation.

The fact that methylene iodide is formed by the action of trisodium arsenite on iodoform is explained by assuming the intermediate formation of sodium di-iodomethylarsonate, thus:

$$CHI_3 + As(ONa)_3 = CHI_2\cdot AsO(ONa)_2 + NaI,$$

which then decomposes into methylene iodide and sodium arsenate (this vol., i, 13). Details are given for the preparation of methylene iodide by this method.

J. C. C.

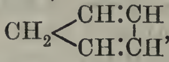
Conversion of *cyclo*Pentene into the Mono- and Di-aldehydes of Glutaric Acid. CARL D. HARRIES and LUDWIG TANK (*Ber.*, 1908, 41, 1701—1711).—In a future communication, the authors will give a comparison of the stability of different ring systems, based on the rate of decomposition of ozonides by water. The present paper deals with *cyclo*pentene, the ozonide of which is readily decomposed by water, whilst that of *cyclo*hexene is only decomposed with difficulty, although the stability of the two ring systems should be of the same order according to the tension theory of Baeyer.

It is very probable that only those aliphatic compounds which contain two carbonyl groups in the β-position to one another are capable of existing in the enolic form, since such compounds are very rarely obtained by the decomposition of ozonides, the substance in its enolic form undergoing further oxidation. *cyclo*Pentene, b. p. 45—46°, D_4^{14} 0·7754, n_D^{14} 1·42080, obtained by the distillation of *cyclo*pentanol with phosphoric oxide, yields when ozonised in excess of cold hexane a viscous *ozonide*, $C_5H_8O_3$, which has the usual odour and properties of such compounds. It is rapidly attacked by boiling water, yielding hydrogen peroxide, glutaric acid, glutardialdehyde, and γ-aldehydobutyric acid.

Glutardialdehyde, $CHO{\cdot}[CH_2]_3{\cdot}CHO$, b. p. 71—72°/10 mm. or 187—189°/760 mm., is a colourless, mobile liquid, which resembles succindialdehyde in many respects (this vol., i, 133). In the presence of a trace of water, it changes into a "glassy" polymeride, which reverts to the unimolecular form by distillation in a vacuum. It has D_4^{20} 1·1238 and n_D^{20} 1·45523, and the molecular refraction indicates that the substance is a true dialdehyde. The *bisnitrophenylhydrazone* has m. p. 79—80°.

γ-*Aldehydobutyric acid*, $CHO{\cdot}[CH_2]_3{\cdot}CO_2H$, b. p. 240°/760 mm. or 136—138°/9 mm., is a viscous liquid with a strongly acid reaction, which reduces ammoniacal silver and Fehling's solutions, is resinified by sodium hydroxide, and very readily oxidises to glutaric acid. It has $D_4^{18\cdot5}$ 1·1657, $n_D^{18\cdot5}$ 1·44973, and the molecular refraction indicates that the substance is a true aldehyde. The high dielectric constant, 23·86 (aniline = 7·2), indicates that the aldehydic character is more pronounced than the acid. The *oxime* has m. p. 110—111°, or, after repeated crystallisation from water, 107—108°. The *semicarbazone* has m. p. 165—166° (decomp.), and the *nitrophenylhydrazone*, 148·5°. The analyses of these three compounds are not very accurate.

*cyclo*Heptene, D_4^{20} 0·823, n_D^{20} 1·45301, ozonised in carbon tetrachloride, yields a viscous, and in some cases a solid, *ozonide*, the analyses of which give numbers between $C_7H_{12}O_3$ and $C_7H_{12}O_4$. The ozonide is decomposed only slowly by boiling water, but the amount is too small to allow of the identification of the products. C. S.

Addition of the Higher Oxides to Doubly Unsaturated Hydrocarbons. A New Case of Addition in the 1 : 4-Position. HEINRICH WIELAND and HANS STENZL (*Annalen*, 1908, 360, 299—322).—As the evidence in favour of Thiele's theory of conjugated linkings has consisted so far chiefly in the addition of hydrogen, bromine, and hydrohaloids, it seemed of importance to study the behaviour of conjugated linkings towards other addenda. Moreover, the investigation of the positions assumed by the group NO_2, on addition to conjugated ethylene linkings, offered some points of interest in connexion with previous studies on the form in which the higher oxides of nitrogen combine with unsaturated compounds (Abstr., 1904, i, 54, 415, 596; 1905, i, 706). The authors have therefore investigated the constitution of the compounds formed by addition of NO_2 groups to $\alpha\delta$-diphenylbutadiene, $CHPh{:}CH{\cdot}CH{:}CHPh$ (compare this vol., i, 35), *cyclo*pentadiene,  $CH_2<\begin{array}{l}CH{:}CH\\ CH{:}CH\end{array}$, and di*cyclo*pentadiene, the constitution of which has not as yet been established.

The following new evidence is brought forward in favour of the formulation of the additive compound of $\alpha\delta$-diphenylbutadiene and nitric peroxide as $\alpha\delta$-dinitro-$\alpha\delta$-diphenyl-Δ^{β}-butylene.

On reduction with the usual reagents and in the ordinary way, the dinitro-compound forms $\alpha\delta$-diphenylbutadiene, a reaction further exemplifying the analogy of the behaviour of the nitro-group with that of the halogens, but, on reduction with zinc and hydrochloric acid under special conditions, it yields small amounts of *diphenylbutadienediamine*, $NH_2{\cdot}CHPh{\cdot}CH{:}CH{\cdot}CHPh{\cdot}NH_2$, which crystallises in colourless needles, m. p. 149° (decomp.), decolorises permanganate in acid solution, and when treated with nitrous acid evolves nitrogen and yields an *oil*. The diamine forms colourless, crystalline *salts* with acetic and hydrochloric acids, and a *picrate*, $C_{16}H_{18}N_2,2C_6H_3O_7N_3$, yellow needles, decomp. about 220°. When suspended in chloroform, cooled by ice, and oxidised with ozone, the dinitro-compound yields large amounts of nitrophenylmethane, $CH_2Ph{\cdot}NO_2$, the decomposition product of nitrophenylacetic acid, $NO_2{\cdot}CHPh{\cdot}CO_2H$, together with small amounts of benzoic acid and benzaldehyde, arising probably from the intermediate formation of α-nitro-$\alpha\delta$-diphenylbutadiene. If the additive compound was $\alpha\beta$-dinitro-$\alpha\delta$-diphenyl-Δ^{γ}-butylene, oxidation would lead to the formation of a dinitro-carboxylic acid, $NO_2{\cdot}CHPh{\cdot}CH(NO_2){\cdot}CO_2H$.

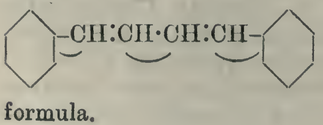
α-Nitro-$\alpha\delta$-diphenylbutadiene forms a *dibromide*,

$$NO_2{\cdot}CPh{:}CH{\cdot}CHBr{\cdot}CHBrPh,$$

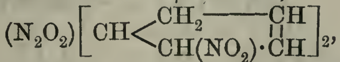
which crystallises in yellow needles, m. p. 106°, decomp. about 165°, and gives a cherry-red coloration with concentrated sulphuric acid.

When suspended in cooled ether and treated with nitrous gas, α-phenylcinnamenylacrylic acid, $CHPh{:}CH{\cdot}CH{:}CPh{\cdot}CO_2H$, evolves carbon dioxide and yields a *dinitro*-compound, which is probably *$\beta\gamma$-dinitro-$\alpha\delta$-diphenylbutadiene*, $CHPh{:}C(NO_2){\cdot}C(NO_2){:}CHPh$; this crystallises in yellow prisms, m. p. 218°, is stable towards acids or cold alkalis, and does not form an additive compound with bromine.

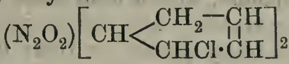
The bearing of these facts on the nature of the ethylene linkings in diphenylbutadiene is discussed. It is considered that the partial valencies of the α- and δ-carbon atoms are neutralised by those of the benzene rings, the behaviour of the compound being best expressed by the annexed formula.



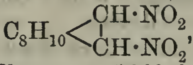
The action of nitrogen trioxide on *cyclo*pentadiene in ethereal solution leads to the formation of a *ψ-nitrosite*,



$$(N_2O_2)\left[CH<\begin{array}{l}CH_2\text{——}CH\\ CH(NO_2)\cdot CH\end{array}\right]_2,$$

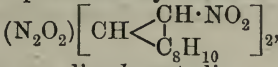
which is obtained in yellow crystals, m. p. 38°, decomposes slightly above its m. p., readily polymerises, gives Liebermann's reaction, and is converted by amyl nitrite and alcoholic hydrogen chloride into the *nitrosochloride*,  $(N_2O_2)\left[CH<\begin{array}{l}CH_2-CH\\ CHCl\cdot CH\end{array}\right]_2$; this crystallises in colourless needles, detonates at about 142°, decolorises permanganate, forms potassium chloride with potassium hydroxide in methyl-alcoholic solution, and gives an orange coloration with phenol and concentrated sulphuric acid.

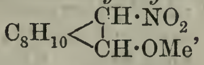
The action of nitrogen dioxide on di*cyclo*pentadiene in ethereal solution leads to the formation of the *dinitro*-compound,



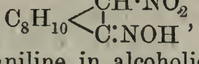
$$C_8H_{10}<\begin{array}{l}CH\cdot NO_2\\ CH\cdot NO_2\end{array},$$

which crystallises in needles, m. p. 122°, is readily attacked by permanganate, does not give Liebermann's reaction, forms a crystalline *dibromide*, and loses 1 mol. of hydrogen nitrite when boiled with alcohol, or alcoholic potassium hydroxide or ammonia.

The *ψ-nitrosite*,  $(N_2O_2)\left[CH<\begin{array}{l}CH\cdot NO_2\\ C_8H_{10}\end{array}\right]_2$, formed by the action of nitrogen trioxide on di*cyclo*pentadiene, crystallises in hexagonal leaflets, m. p. 144—146° (decomp.), forms green solutions, reacts slowly with permanganate, does not give Liebermann's reaction, and when boiled with potassium in methyl-alcoholic solution evolves nitrous oxide and forms *nitromethoxydihydrodi*cyclo*pentadiene*,



$$C_8H_{10}<\begin{array}{l}CH\cdot NO_2\\ CH\cdot OMe\end{array},$$

which crystallises in rhombohedra, m. p. 68°, gives a blood-red coloration with alcoholic ferric chloride, forms *precipitates* with zinc, silver, and copper salts in neutral solution, and reacts slowly with permanganate. The *nitro-oxime*,  $C_8H_{10}<\begin{array}{l}CH\cdot NO_2\\ C{:}NOH\end{array}$, formed by boiling the ψ-nitrosite with alcohol or aniline in alcoholic solution, crystallises from benzene in prisms or needles, m. p. 138—139°, gives an intense green coloration with ferric chloride, and yields hydroxylamine when boiled with 20% sulphuric acid. G. Y.

Compounds of Platinous Chloride with Di*cyclo*pentadiene. Karl A. Hofmann and J. von Narbutt (*Ber.*, 1908, 41, 1625—1628). —It has been already found that mercuric chloride, di*cyclo*pentadiene, and alcohols give compounds of the class $HgCl\cdot C_{10}H_{12}\cdot OR$ (Hofmann and Seiler, Abstr., 1906, i, 786), and it has since been discovered that platinous chloride in aqueous alcohols reacts in a similar way to form the stable ethers, $PtCl\cdot C_{10}H_{12}\cdot OR$.

*Chloroplatomethoxydi*cyclo*pentadiene*, $PtCl\cdot C_{10}H_{12}\cdot OMe$, obtained by mixing an aqueous solution of potassium platinichloride with a methyl-alcoholic solution of di*cyclo*pentadiene, crystallises in pale yellow plates, decomp. 190°. At 15°, the experiment requires several weeks; at 40°, several days. Hot potassium hydroxide decomposes it into hydrocarbon, and 20% hydrochloric acid at 15° slowly converts the plates into prisms, probably the compound $PtCl\cdot C_{10}H_{12}Cl$. The *ethoxy-compound*, $PtCl\cdot C_{10}H_{12}\cdot OEt$, forms pale yellow prisms; propyl alcohol does not give an analogous compound, but the *compound*, $PtCl\cdot C_{10}H_{12}Cl$, which separates in needle aggregates. The conclusion is drawn that these compounds owe their stability partly to their containing the linking $ClPt\cdot\overset{|}{C}H\cdot\overset{|}{C}H\cdot Cl$ or OMe. W. R.

The Optical Behaviour of *cyclo*Hexadiene Derivatives. Karl Auwers (*Ber.*, 1908, **41**, 1828—1831. Compare Abstr., 1906, i, 947; Brühl, Trans., 1907, **91**, 115).—The author draws attention to the fact that many *cyclo*hexadienes which contain conjugated ethylene linkings do not show the exaltation in molecular refraction and dispersion usually characteristic of such compounds. It is pointed out that many of these unsaturated hydrocarbons tend to polymerise, and that determinations should be made with freshly-prepared specimens. the low values obtained for some of the compounds may possibly be due to the fact that polymerised products were examined.

Methyl 1 : 4-dimethyl-$\Delta^{1,3}$-hexadiene-2-carboxylate also does not exhibit the usual exaltation. J. J. S.

Dihydrotoluene ($\Delta^{1:3}$-Methyl*cyclo*hexadiene). Carl D. Harries (*Ber.*, 1908, **41**, 1698—1701).—The dihydrotoluene obtained by the dry distillation of hexahydro-*m*-tolylenediamine phosphate (Abstr., 1901, i, 194; 1902, i, 361) yields by suitable oxidation with potassium permanganate the same 1 : 2-dihydroxymethyl*cyclo*hexane-3-one as is obtained from methyl*cyclo*hexenone (Abstr., 1898, i, 402), and is consequently $\Delta^{1:3}$-methyl*cyclo*hexadiene. Klages found, however (Abstr., 1907, i, 597), that the observed and calculated molecular refractions agreed, although it is well known that substances containing a conjugated double linking exhibit an exhaltation of this constant. The author has therefore redetermined the physical constants of this dihydrotoluene, and, with D_4^{20} 0·8354 and n_D^{20} 1·47628, the observed molecular refraction, 31·72, shows a small increment over the calculated value, 31·43. This result points to the presence in the dihydrotoluene of an isomeride which does not contain a conjugated double linking. Evidence in the same direction is obtained by the action of bromine, more than one molecular proportion of the halogen being absorbed. The action of ozone on dihydrotoluene gives a gelatinous product, which is apparently a mixture of a mono- and a di-ozonide, but the decomposition of the substance by water does not give conclusive results as to its structure. C. S.

Contact Oxidation of Hydrocarbons. E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 652—658. Compare this vol., i, 306).—The author has investigated the oxidation of various hydrocarbons under the conditions of the former experiments (*loc. cit.*).

With light petroleum, D 0·71, the gaseous products of oxidation included 8—10% of carbon dioxide and 6·8—2·4% of carbon monoxide, other products being about 10% of close-chain and ethylene hydrocarbons of the compositions C_6H_{12} and C_5H_{10}. Further aldehydic derivatives of the benzene series with the aldehyde group in the meta- or para-position were also obtained. Heavier oils yield similar products.

Benzene yields (1) a gaseous product containing 12·44% of carbon dioxide, 2·44% of oxygen, 6·78% of carbon monoxide, 6·94% of methane, and 71·4% of nitrogen; (2) aldehydic and carboxylic derivatives of benzene. From a study of the various products, the author concludes that the benzene undergoes a series of condensations and oxidations; for instance, $2C_6H_6 = H_2 + C_6H_5{\cdot}C_6H_5$ (the latter being then oxidised to "acroleïnphenol," benzaldehyde, and a hydroxybenzoic acid) and $3C_6H_6 = 2H_2 + C_6H_5{\cdot}C_6H_4{\cdot}C_6H_5$, the latter being then transformed into hydroxydiphenylcarboxylic acid or the corresponding aldehyde.

Toluene yields, in addition to the gaseous products, 2·5—4% of benzaldehyde and various substances with reducing and phenolic properties, and similar to the corresponding products obtained from benzene.

In the case of turpentine, the gas obtained has the following composition: CO_2, 7·55%; O, 1·77%; CO, 7·55%; H, 4·8%; CH_4, 3·6%; C_2H_4, 1·2%; N, 73·5%. The other products obtained indicate that the turpentine loses part of its hydrogen and condenses to hydrocarbons of the diphenyl series, the latter then undergoing oxidation as in the case of benzene (*vide supra*).

The results so far obtained indicate that many gases, for example, natural methane and illuminating gas, may be converted by contact oxidation into more valuable products, such as formaldehyde.

T. H. P.

1:2-Dibromo-3-nitrobenzene and the Nitration of *o*-Dibromobenzene. ARNOLD F. HOLLEMAN [with P. C. J. EUWES] (*Rec. trav. chim.*, 1908, **27**, 153—161. Compare Abstr., 1906, i, 345).—An improved method for the preparation of 1:2-dibromo-3-nitrobenzene from *o*-nitroaniline is described.

The m. p. previously ascribed to this compound (*loc cit.*) is too low. When crystallised from light petroleum, it has m. p. 84—85°. Pure *o*-dibromobenzene, m. p. 5·6°, has been treated at 0° with nitric acid (D 1·5). By an examination of the solidifying point and density, the product of nitration is found to consist of 84% 1:2-dibromo-4-nitrobenzene with 16% 1:2-dibromo-3-nitrobenzene. These two isomerides cannot be separated by fractional crystallisation. W. O. W.

Halogen Derivatives of Dinitrohydrocarbons. GIACOMO PONZIO and G. CHARRIER (*Atti R. Accad. Sci. Torino*, 1908, **43**, 475—482; *Gazzetta*, 1908, **38**, i, 648—654).—Whereas two forms of ω-nitrotoluene are known having the structures $CH_2Ph{\cdot}NO_2$ and $CHPh{:}NO{\cdot}OH$ respectively, only one form of ω-dinitrotoluene,

$$CHPh(NO_2)_2,$$

has been obtained (compare Ponzio, Abstr., 1906, i, 735, and Hantzsch, Abstr., 1906, i, 500); two potassium salts of ω-dinitrotoluene are, however, known, one colourless and probably having the structure $NO_2{\cdot}CPh{:}NO{\cdot}OK$, and the other yellow and capable of being represented by two formulæ, $OK\cdot N{:}CPh\cdot O\cdot NO_2$ and $OK\cdot CPh(NO_2)\cdot NO$. The nature of the product of the action of hypochlorites on the yellow salt is in favour of the latter structure, a chlorine derivative being obtained which probably has the constitution $NO\cdot CPh(NO_2)\cdot OCl$, as it gives with alcoholic potash, potassium nitrate, nitrite, and benzoate in addition to the potassium salt of ω-dinitrotoluene. The alternative formula $CPhCl(NO_2)_2$ does not so well explain the facts. The yellow diazobenzene derivative obtained by the action of diazobenzene acetate on the yellow potassium salt of ω-dinitrotoluene is therefore probably $NO\cdot CPh(NO_2)\cdot O\cdot N{:}NPh$, a formula which is in good accord with the easy transformation of the substance into nitronitrosobenzoylphenylhydrazine, $NO_2\cdot NBz\cdot NPh\cdot NO$ (compare this vol., i, 482).

ω-*Chlorodinitrotoluene*, $CPCl_2No_4$, separates immediately on adding a dilute solution of potassium ω-dinitrotoluene to an alkaline solution of chlorine at 0° as a colourless oil which is stable under ordinary conditions; when warmed with water, it gives benzoic acid and nitrous fumes.

ω-*Bromodinitrotoluene*, obtained similarly, is a slightly yellow oil. The *phenylhydrazine* salt, $CHPhN_2O_4,PhN_2H_3$, of ω-dinitrotoluene, obtained by mixing aqueous solutions of potassium ω-dinitrotoluene and phenylhydrazine hydrochloride, forms yellow leaflets, m. p. 87°.

ω-*Chlorodinitroanisole*, $OMe\cdot C_6H_4\cdot CClN_2O_4$, and ω-*bromodinitroanisole*, prepared from ω-dinitroanisole, are colourless oils, which are stable at the ordinary temperature and give anisic acid when boiled with water; alcoholic potash converts both substances into potassium ω-dinitroanisole. The *phenylhydrazine* salt of ω-dinitroanisole forms yellow leaflets, m. p. 79°.

ω-*Chlorodinitro*-3 : 4-*methylenedioxytoluene*, $CH_2O_2{:}C_6H_3\cdot CClN_2O_4$, prepared from ω-dinitro-3 : 4-methylenedioxytoluene, crystallises from alcohol in large, slightly yellow plates, m. p. 55°; ω-*bromodinitro*-3 : 4-*methylenedioxytoluene*, m. p. 81°, crystallises from light petroleum.

W. A. D.

Reduction of Nitro-compounds by Zinin's Method. RICHARD WILLSTÄTTER and HEINRICH KUBLI (*Ber.*, 1908, **41**, 1936—1940).—The authors find that when aromatic nitro-compounds are treated in alcoholic solution with ammonium sulphide in the cold, good yields of the corresponding aryl-hydroxylamines are obtained. From nitrobenzene was prepared phenylhydroxylamine; from *p*-nitrotoluene, *p*-tolylhydroxylamine, and α-nitronaphthalene gave α-naphthylhydroxylamine.

The latter crystallises with $1H_2O$, forming colourless, glistening prisms, m. p. 79° (compare Scheiber, Abstr., 1904, i, 867). The anhydrous substance has the same m. p. When α-naphthylhydroxylamine is dissolved in anhydrous ether and shaken with dry silver oxide in presence of anhydrous copper sulphate or sodium sulphate, it yields α-nitrosonaphthalene in clear yellow crystals dissolving to a green solution. When heated, α-nitrosonaphthalene turns green at 80°, and has m. p. 85—86°; it then solidifies, and has m. p. 98°. J. C. C.

Picrates. WILHELM SUIDA (*Ber.*, 1908, **41**, 1909—1913).—Anthranilic acid forms two picrates, $C_7H_7O_2N,C_6H_3O_7N_3$, yellowish-brown prisms, and $2C_7H_7O_2N,C_6H_3O_7N_3$, red, or when containing $1\frac{1}{2}H_2O$ yellow, crystals, depending on the proportions in which concentrated solutions of anthranilic and picric acids are mixed. In the same manner, *p*-toluidine and picric acid combine in the molecular proportion 1 : 1, forming a brownish-yellow, or in the proportion 2 : 1, forming a bright yellow, salt.

α-Naphthylamine also forms a greenish-yellow picrate containing 1 mol., and a copper-red picrate containing 2 mols., of the base and 1 mol. of picric acid. Aniline, on the other hand, forms only one brownish-yellow picrate. G. Y.

Tri-*p*-halogen Substitution Products of Triphenylmethane and Triphenylcarbinol. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 789—798. Compare Abstr., 1907, i, 1050).—Crystallographical determinations with the following substances: tri-*p*-iodotriphenylmethane, rhombic [$a : b : c = 0·5765 : 1 : 0·8798$]; tri-*p*-iodotriphenylmethane containing benzene of crystallisation, triclinic [$a : b : c = 0·5719 : 1 : 1·4298$; $\alpha = 109°8'$; $\beta = 126°21'$; $\gamma = 107°32'$]; tri-*p*-chlorotriphenylcarbinol, rhombic [$a : b : c = 0·6009 : 1 : 0·9781$]; tri-*p*-bromotriphenylcarbinol, rhombic [$a : b : c = 0·8407 : 1 : 0·8081$]; tri-*p*-iodotriphenylcarbinol, rhombic [$a : b : c = 0·8543 : 1 : 0·817$], and tri-*p*-iodotriphenylcarbinol containing benzene of crystallisation, triclinic [$a : b : c = 1·3991 : 1 : 1·6135$; $\alpha = 109°16'$; $\beta = 117°36'$; $\gamma = 62°52'$]. G. Y.

Mercury Salts of the Three Nitroanilines. C. LORING JACKSON and R. W. PEAKES (*Amer. Chem. J.*, 1908, **39**, 567—572).—During a study of the abnormal replacement of bromine by hydrogen in 1 : 3 : 5-tribromo-2 : 4-dinitrobenzene, this substance was treated with the nitroanilines, but reaction did not take place under any conditions. The mercury salts of the nitroanilines were therefore prepared with a view to ascertaining if they would react with 1 : 3 : 5-tribromo-2 : 4-dinitrobenzene, but they gave no better results.

These *salts*, $(NO_2·C_6H_4·NH)_2Hg$, are precipitated when a strong solution of potassium hydroxide is added to a solution of the nitroaniline and mercuric nitrate. The salt of *p*-nitroaniline is crimson, that of the *m*-derivative is maroon-coloured and contains $1H_2O$, and that of the *o*-compound is bright red. The *o*-salt is formed the most rapidly, the *m*-salt next, and the *p*-salt most slowly. E. G.

Action of Bromine or of Sodium Hypobromite on *m*-Nitroaniline and Some of its Halogen Substitution Derivatives. WILHELM KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 465—480).—The authors have studied the action of bromine or sodium hypobromite on *m*-nitroaniline and some of its halogenated derivatives with the hope of obtaining new mono- and di-substituted derivatives of *m*-nitroaniline, and of ascertaining in what order the three hydrogen atoms of *m*-nitroaniline, capable of substitution, are replaced by the halogen.

Bromination of *m*-nitroaniline with bromine in chloroform solution yields tribromo-*m*-nitroaniline, m. p. 102·5°, *p*-bromo-*m*-nitroaniline, and a small quantity of 2 : 4-dibromo-5-nitroaniline (*vide infra*).

Bromination of *m*-nitroaniline (1 mol.) with sodium hypobromite (1 atom of bromine) in acetic acid solution gives (1) 4-bromo-3-nitroacetanilide; (2) 2-*bromo*-5-*nitroacetanilide*, $NHAc\cdot C_6H_3Br\cdot NO_2$, which crystallises from alcohol in slender, monoclinic needles or prisms [Artini : $a:b:c = 3·3702:1:1·2522$; $\beta = 77°3'$], m. p. 180°, D 1·831. When treated with concentrated sulphuric acid at 120°, it is converted into 2-*bromo*-5-*nitroaniline*, $NH_2\cdot C_6H_3Br\cdot NO_2$, which crystallises from alcohol in orange-yellow needles, m. p. 141°.

The action of sodium hypobromite on *p*-bromo-*m*-nitroaniline in acetic acid solution yields : (1) 2 : 4-*dibromo*-5-*nitroacetanilide*,

$$NHAc\cdot C_6H_2Br_2\cdot NO_2,$$

which crystallises from ethyl acetate in flattened needles or long plates, m. p. 172°, and can also be obtained, mixed with 2 : 4-dibromo-6-nitroacetanilide, by nitrating 2 : 4-dibromoacetanilide in sulphuric acid. De-acetylation of this compound yields 2 : 4-*dibromo*-5-*nitroaniline*, $NH_2\cdot C_6H_2Br_2\cdot NO_2$, which crystallises from alcohol in slender, pale yellow, monoclinic laminæ [Artini : $a : b : c = 2·1598 : 1 : 3·0212$; $\beta = 73°51'$], m. p 114·2°. (2) 2 : 4-*Dibromo*-3-*nitroacetanilide*,

$$NHAc\cdot C_6H_2Br_2\cdot NO_2,$$

which crystallises from benzene in slender, white needles, m. p. 150°. When treated with nitrous acid, it is converted into 1 : 3-dibromo-2-nitrobenzene, which may be prepared conveniently in this way.

When 1 : 3-dibromo-2-nitrobenzene is treated with nitric acid, D 1·54, it yields 1 : 3-*dibromo*-2 : 4-*dinitrobenzene*, $C_6H_2Br_2(NO_2)_2$, which crystallises from alcohol in long, almost colourless needles or in yellowish-green plates, m. p. 83°, and, under the action of alcoholic ammonia solution, is converted into 2 : 4-*dinitrophenylene*-1 : 3-*diamine*, $C_6H_2(NH_2)_2(NO_2)_2$, which crystallises from alcohol in orange-yellow needles, m. p. 250°. When treated with potassium hydroxide solution, the latter yields the potassium salt of 2 : 4-dinitroresorcinol, $C_6H_2(OK)_2(NO_2)_2$.

Nitration of 1 : 3-dibromo-2-nitrobenzene with excess of nitric acid, or with a mixture of nitric and sulphuric acids, results in the formation of 1 : 3-dibromo-2 : 4 : 6-trinitrobenzene, which, when treated with alcoholic ammonia solution, yields 2 : 4 : 6-trinitrophenylene-1 : 3-diamine (compare Noelting and Collin, Abstr., 1884, 1004). The latter, under the action of dilute potassium hydroxide solution, gives potassium styphnate.

Reduction of 1 : 3-dibromo-2-nitrobenzene with tin and hydrochloric acid, and replacement of the amino-group of the resultant product by bromine, leads to the formation of 1 : 2 : 3-*tribromobenzene*, $C_6H_3Br_3$, which crystallises in colourless, monoclinic plates

$$[a : b : c = 1·5490 : 1 : 1·8516;\ \beta = 113°7'30''],$$

m. p. 87·4°, D 2·658. 2-*Chloro*-1 : 3-*dibromobenzene*, $C_6H_3ClBr_2$, obtained in a similar manner, m. p. 73°, and 2-*iodo*-1 : 3-*dibromobenzene*, $C_6H_3Br_2I$, m. p. 99·8°, crystallise in forms similar to that of the tribromo-derivative. 2 : 6-*Dibromoacetanilide*, $C_6H_3Br_2{\cdot}NHAc$, crystallises from alcohol in colourless, trimetric prisms

$$[a:b:c=0{\cdot}734:1:0{\cdot}392],$$

m. p. 210°, D_{16} 1·923.

The action of sodium hypobromite on *p*-chloro-*m*-nitroaniline in acetic acid yields (1) 4-*chloro*-2-*bromo*-5-*nitroacetanilide*,

$$NHAc{\cdot}C_6H_2ClBr{\cdot}NO_2,$$

which crystallises from alcohol in long, white needles, m. p. 147·4°, and is also obtained by nitrating 4-chloro-2-bromoacetanilide in sulphuric acid solution. The corresponding 4-*chloro*-2-*bromo*-5-*nitroaniline*, $NH_2{\cdot}C_6H_2ClBr{\cdot}NO_2$, crystallises from alcohol in yellow, monoclinic prisms [$a:b:c=2{\cdot}1321:1:3{\cdot}0222$; $\beta=73°17'$], m. p. 108°, D 1·739. Replacement of the amino-group in this compound by hydrogen gives 1-*chloro*-3-*bromo*-6-*nitrobenzene*, m. p. 42·4° (compare Körner, this Journ., 1876, i, 204). (2) 4-*Chloro*-2-*bromo*-3-*nitroacetanilide*, $NHAc{\cdot}C_6H_2ClBr{\cdot}NO_2$, which crystallises from aqueous alcohol in colourless plates or faintly yellow prisms, m. p. 135—136°. The corresponding 4-*chloro*-2-*bromo*-3-*nitroaniline*, $NH_2{\cdot}C_6H_2ClBr{\cdot}NO_2$, m. p. 99—100°, is similar in crystalline habit and chemical properties to the analogous dibromonitroaniline.

2-Bromo-5-nitroaniline is converted quantitatively into 2 : 4-dibromo-5-nitroaniline on bromination.

These results show that, in the bromination of *m*-nitroaniline, the positions accessible to the halogen are the para-position and, in a less degree, the ortho-position non-adjacent to the nitro-group ; in no case does the halogen enter the meta-position. When the para-position in *m*-nitroaniline is already occupied by a halogen atom, the new halogen atom assumes indifferently either of the two ortho-positions. If the ortho-position is occupied, the halogen atom assumes the para-position.

Partial bromination of 3 : 5-dinitroaniline yields (1) 2-*bromo*-3 : 5-*dinitroaniline*, $NH_2{\cdot}C_6H_2Br(NO_2)_2$, which crystallises from alcohol in golden-yellow laminæ, m. p. 181°, and, on treatment with alcoholic ammonia solution gives 3 : 5-dinitrophenylene-1 : 2-diamine (compare Nietzki and Hagenbach, Abstr., 1897, i, 277), m. p. 215°. (2) 2 : 4 : 6-Tribromo-3 : 5-dinitroaniline (compare Blanksma, *Rec. trav. chim.*, 1902, 21, 255). T. H. P.

Preparation of *o*-Nitroamines from the Corresponding Phenol Derivatives. FRITZ ULLMANN and GÉZA NÁDAI (*Ber.*, 1908, 41, 1870—1878).—The authors find that when arylsulphonic esters of *o*-nitrophenol and its derivatives are treated with amines, they are converted into the corresponding *o*-nitroamines. Aniline acts only slowly on the ester of *o*-nitrophenol, but the reaction proceeds very quickly when the ester of 2 : 4-dinitrophenol is employed, thus :

$$C_6H_3(NO_2)_2{\cdot}O{\cdot}SO_2{\cdot}C_7H_7+2NH_2Ph=C_6H_3(NO_2)_2{\cdot}NHPh+NH_2Ph,C_7H_7{\cdot}SO_3H.$$

It was not found possible to prepare the arylsulphonic ester of picric acid, and in presence of pyridine, quinoline, or diethylaniline, picryl chloride was obtained. 2 : 4-Dinitrophenol, when treated with toluenesulphonyl chloride and diethylaniline, also gave a mixture of chlorodinitrobenzene and the sulphonic ester, but *o*- and *p*-nitrophenols gave, under the same conditions, only the corresponding esters, whilst benzoic and cinnamic acids furnished the corresponding acid chlorides.

The 2 : 4-*dinitrophenyl* ester of p-*toluenesulphonic acid* crystallises from alcohol or glacial acetic acid in colourless prisms, m. p. 121°. When treated with gaseous ammonia in boiling nitrobenzene solution, it gives ammonium toluenesulphonate and 2 : 4-dinitroaniline, and, when warmed with aniline, 2 : 4-dinitrodiphenylamine is obtained. On reduction, the dinitro-ester gives the 2 : 4-*diaminophenyl* ester of p-*toluenesulphonic acid*, white leaflets, m. p. 125°; the *diacetyl* derivative, white needles, m. p. 167°. The dinitro-ester with pyridine gives *dinitrophenylpyridinium toluenesulphonate*, $C_{18}H_{15}O_7N_3S$, white needles.

When picric acid is heated with toluenesulphonyl chloride in presence of diethylaniline and nitrobenzene, and the product poured into ammonia, picramide is formed; when aniline is employed instead of ammonia, 2 : 4 : 6-trinitrodiphenylamine results, and with *p*-toluidine, 2 : 4 : 6-*trinitrophenyl*-p-*tolylamine*, red needles, m. p. 169°, is obtained. The 3 : 5-*dinitrotolyl* ester of p-*toluenesulphonic acid*, prepared from 3 : 5-dinitro-*p*-cresol and the acid chloride, feathery needles, m. p. 154°, when warmed with aniline in benzene solution gives *phenyl*-2 : 6-*dinitro*-p-*tolylamine*, orange leaflets, m. p. 174°.

Trinitro-*m*-cresol, when condensed with *p*-toluenesulphonyl chloride in presence of diethylaniline, yields 3-chloro-2 : 4 : 6-trinitrotoluene (Reverdin, Dresel, and Delétra, Abstr., 1904, i, 580). J. C. C.

A Violet *aci*-Ether of Hexanitrodiphenylamine. ARTHUR HANTZSCH and ST. OPOLOSKI (*Ber.*, 1908, 41, 1745—1749).—It has been found possible to isolate a *aci*-methyl ether of hexanitrodiphenylamine. The compound is deep violet in colour, and corresponds with the red *aci*-ethers of the nitrophenols.

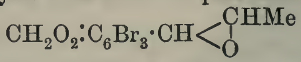
The constitutional formula $C_6H_2(NO_2)_3\cdot N{:}C_6H_2(NO_2)_2{:}NO\cdot OMe$ is suggested, whereas the ordinary yellow methyl ether is regarded as the *N*-ether, $C_6H_2(NO_2)_3\cdot NMe\cdot C_6H_2(NO_2)_3$.

The *silver* derivative of hexanitrodiphenylamine is obtained most readily by the action of silver oxide on an acetone solution of the nitro-compound and subsequent precipitation with ether. It forms brilliant violet crystals, and decomposes above 200°. The salt reacts with a benzene solution of acetyl chloride, yielding the pale yellow *acetyl* derivative, $C_6H_2(NO_2)_3\cdot NAc\cdot C_6H_2(NO_2)_3$, m. p. 240° (decomp.). The *N*-methyl and ethyl ethers are both yellow (compare Mulder, Abstr., 1906, i, 493), and give a red coloration with dilute alkalis only after hydrolysis. The ethers cannot be obtained by the action of picryl chloride or alkyl derivatives of picramide. A small amount of the violet *aci*-methyl ether (*O*-ether) is obtained when the dry silver salt is treated with excess of methyl iodide at 0° without the addition of a solvent. It crystallises from an absolutely dry mixture of benzene and hexane in black needles; it melts and decomposes at 140—141° when heated rapidly, or at 120° when heated slowly. Its solutions in benzene have a violet colour, and are comparatively stable.

The acetone solution is very unstable, and readily yields hexanitrodiphenylamine. J. J. S.

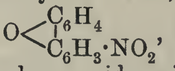
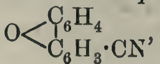
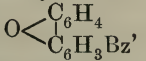
Mutual Solubility of Solid Aromatic and the Corresponding Hexahydrogenated Compounds (Equilibrium in the System: Phenol–*cyclo*Hexanol.) Luigi Mascarelli aud Ugo Pestalozza (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 601—609. Compare Abstr., 1907, ii, 936).—The composition-freezing point diagram for mixtures of phenol and *cyclo*hexanol consists of three branches: (1) from 0 to about 20% of *cyclo*hexanol the freezing point falls continuously from 40° to about 19°; (2) from 20, to about 80—90% it rises slightly at first and afterwards falls rapidly to about −50°; (3) from 80—90 to 100% of *cyclo*hexanol the freezing point rises from about −50° to +20°. In order to ascertain whether the slightly marked maximum of the second branch corresponds with the formation of an additive compound between the phenol and *cyclo*hexanol, the equilibrium was studied in the presence of ethylurethane, which satisfies the conditions laid down by Mascarelli (compare this vol., ii, 94). As the maximum undergoes appreciable displacement towards the ordinate axis, it cannot correspond with an additive compound. On determining the composition of the separated crystals by Bylert's method (Abstr., 1891, 1411), using benzil as third substance, it is found that a solid solution is formed.

The results show that the two substances, phenol and *cyclo*hexanol, are dimorphous, but only one form of the one compound can give solid solutions with one of the other. The ordinary forms of phenol and *cyclo*hexanol are incapable of dissolving in the solid state, and should give a curve consisting of two straight lines, of which the first and third branches of the experimental curve form parts. The other forms of phenol and *cyclo*hexanol are completely soluble in the solid condition, so that they should give a curve rising to a maximum; the second branch of the experimental curve represents part of this ideal curve. The existence of two forms of phenol is in accord with the observations of Tammann (Krystallisieren und Schmelzen, 1903, 308), who gave the m. p. of the unstable form of phenol as about 30°; the authors' results lead to the value 10—20°. T. H. P.

Chlorinating Action of Phosphorus Pentachloride and the Action of Thionyl Chloride on Carbonyl Compounds. Paul Hoering and F. Baum (*Ber.*, 1908, 41, 1914—1918).—When boiled with a mixture of phosphorus tri- and penta-chlorides, *iso*safrole is converted into di*iso*safrole (Angeli and Mola, Abstr., 1895, i, 24). Dibromo- and tribromo-*iso*safrole, on the other hand, when heated with phosphorus pentachloride, form mixtures of stereoisomeric dichlorides, which are separated only partly and with difficulty. From dibromo*iso*safrole there is obtained a *dichloride*, $C_{10}H_8O_2Cl_2Br_2$, m. p. 97—99°, and from the tribromo-compound a crystalline mixture, m. p. 134—145°, from which was isolated a *dichloride*, $C_{10}H_7O_2Cl_2Br_3$, m. p. 173·5—174·5°, or in one case 176—177°. This is stable towards water, but when heated gently with sodium ethoxide yields a crystalline *product*, m. p. 90—90·5°, containing only 1 atom of chlorine, and when boiled with sodium acetate in glacial acetic acid solution is converted into an *acetate*, which, on hydrolysis with alcoholic potassium hydroxide, forms tribromo*iso*safrole oxide,  $CH_2O_2{:}C_6Br_3{\cdot}CH{<}\begin{matrix}CHMe\\|\\O\end{matrix}$; hence the addition of chlorine must have taken place at the ethylene linking in the propenyl side-chain of the *iso*safrole. In agreement with this, it is found that the action of phosphorus pentabromide on di- and tri-bromo*iso*safrole leads to the formation of the dibromides, which are obtained also by direct addition of bromine.

Piperonal dichloride is formed by the action of thionyl chloride on piperonal, and, when heated with phosphorus pentachloride at 110—120°, yields dichloropiperonal dichloride, b. p. 163°/18 mm. (compare Barger, Trans., 1908, 41, 1768). An attempt to found on this a general method of preparing dichlorides by the action of thionyl chloride on aldehydes was unsuccessful. Benzaldehyde, treated with thionyl chloride, yields benzyl chloride almost quantitatively; salicylaldehyde reacts with thionyl chloride or phosphorus pentachloride, forming disalicylide; anisaldehyde under similar conditions yields an unstable *product*, b. p. 125—130°/14 mm., which could not be purified; acetaldehyde and paraldehyde yield a mixture of products, b. p. 118—125°, whilst acetone reacts energetically with thionyl chloride, forming a *product* which decomposes on distillation and does not contain even traces of dichloropropane.

G. Y.

Derivatives of Diphenylene Oxide. WALTHER BORSCHE and W. BOTHE (*Ber.*, 1908, 41, 1940—1944).—Although Galewsky (Abstr., 1891, 1234) was unable to obtain a mononitro-derivative of diphenylene oxide, the authors have prepared 4-*nitrodiphenylene oxide*,  $O{<}\begin{matrix}C_6H_4\\|\\C_6H_3{\cdot}NO_2\end{matrix}$, by warming a glacial acetic acid solution of diphenylene oxide with nitric acid, D 1·52. It crystallises from acetic acid in yellow, silky needles, m. p. 181—182°. On reduction with tin and hydrochloric acid, it yields 4-*aminodiphenylene oxide*, m. p. 94°. The *hydrochloride*, decomp. 220°, the *stannichloride*, the *diacetyl* derivative, colourless needles, m. p. 83°, and the *benzoylamino*-derivative, m. p. 201°, are described. When the *diazo-chloride* is stirred into a solution of sodium sulphide and sodium hydroxide, *sodium diphenylene-oxide-azosulphonate*, $C_{12}H_7O{\cdot}N_2{\cdot}SO_3Na$, separates in yellow crystals. On acidification with acetic acid and treatment with zinc dust, *sodium diphenylene-oxide-hydrazinesulphonate* is formed, which on boiling with hydrochloric acid yields *hydrazinodiphenylene oxide*, $C_{12}H_{10}ON_2$, in leaflets, m. p. 152°. The *hydrochloride* has m. p. 225°. The chloride of diazodiphenylene oxide is not decomposed by boiling a solution with concentrated sulphuric acid; with phenol it forms *phenolazodiphenylene oxide*, reddish-brown crystals, m. p. 199°, and suffers the usual Sandmeyer decomposition, by means of which is obtained 4-*iododiphenylene oxide*, yellow leaflets, m. p. 182°, and the *nitrile*,  $O{<}\begin{matrix}C_6H_4\\|\\C_6H_3{\cdot}CN\end{matrix}$, colourless needles, m. p. 120°, which on hydrolysis furnishes *diphenylene-oxide-4-carboxylic acid*, colourless needles, m. p. 266°. This is also formed by treating acetyldiphenylene oxide (Galewsky, *loc. cit.*) with sodium hypochlorite. *Benzoyldiphenylene oxide*,  $O<\begin{matrix}C_6H_4\\ |\\ C_6H_3Bz\end{matrix}$, obtained from diphenylene oxide by treatment with benzoyl chloride and aluminium chloride, forms white needles, m. p. 167—168°, and gives an *oxime*, m. p. 234—235, the *benzoyl* derivative of which has m. p. 246°. J. C. C.

Hydrogenation of Polyphenols. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, **146**, 1193—1196).—The authors have applied Sabatier and Senderens' method of hydrogenation by means of finely-divided nickel to quinol, catechol, and pyrogallol. At 160—170°, quinol yields a mixture of phenol, *cyclo*hexanol, and *cis-* and *trans-cyclo*hexane-1 : 4-diols. At 130°, the *cis*-compound is obtained exclusively. Catechol gives cis-cyclo*hexane*-1 : 2-*diol*, rhombic crystals, m. p. 75—76°, b. p. about 225°. Pyrogallol is converted into cyclo*hexane*-1 : 2 : 3-*triol*, tabular crystals, m. p. 67°. No definite product could be obtained from resorcinol, although a very small amount of a substance, m. p. 65°, was isolated, which was probably *cis-cyclo*hexane-1 : 3-diol. J. C. C.

Melting Point of Resorcinol. CHARLES T. BENNETT (*Pharm. J.*, 1908, [iv], **26**, 758).—After repeated crystallisation from benzene, resorcinol has m. p. 110°, although higher figures (up to 119°) are given in the literature. The sample was pure as estimated by Richard's method (titration with *N*/5-iodine), and contained neither catechol nor quinol. J. C. C.

Guaiacylphosphoric Acids. VICTOR AUGER and P. DUPUIS (*Compt. rend.*, 1908, **146**, 1151—1153).—The authors have prepared mono- and di-guaiacylphosphoric acids by the following three methods: (1) by boiling guaiacol with phosphoryl chloride, and hydrolysing the resulting guaiacylphosphoryl dichloride and diguaiacylphosphoryl chloride; (2) by treating a mixture of guaiacol and pyridine in the cold with phosphoryl chloride, and decomposing the pyridine salt with alkali (especially suitable for the preparation of diguaiacylphosphoric acid), and (3) by hydrolysing guaiacol phosphate with the calculated amount of alcoholic soda. *Guaiacylphosphoryl dichloride*,

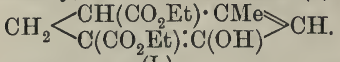
$$OMe\cdot C_6H_4\cdot O\cdot POCl_2$$

is a colourless oil, b. p. 178—180°/30 mm., readily hydrolysed to *monoguaiacylphosphoric acid*, slender, deliquescent needles, m. p. 94°. The alkali salts are soluble in water, and the salts of the alkaline earths and of the heavy metals are insoluble; the *sodium*, *calcium*, and *copper* salts are described. *Diguaiacylphosphoryl chloride*,

$$(OMe\cdot C_6H_4\cdot O)_2POCl,$$

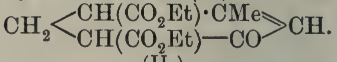
is a colourless oil, b. p. 258°/15 mm., slowly hydrolysed by water to *diguaiacylphosphoric acid*, colourless tablets, m. p. 97°. The *sodium*, *calcium*, and *copper* salts are described. The two latter are soluble in water, and may be used for the separation of mono- and di-guaiacylphosphoric acids, as the corresponding salts of the mono-acid are insoluble. The authors find that when guaiacol is heated with phosphoryl chloride and excess of pyridine, the methyl group is eliminated with formation of catechol. J. C. C.

Tautomerism. IV. PAUL RABE (*Annalen*, 1908, **360**, 289—298. Compare Abstr., 1906, i, 89).—The author finds that ethyl methyl*cyclo*hexenonedicarboxylate exists in two desmotropic modifications, namely, a solid enolic form (I) and an oily ketonic form (II):



$$CH_2<\begin{matrix}CH(CO_2Et)\cdot CMe\\C(CO_2Et):C(OH)\end{matrix}>CH.$$

(I.)



$$CH_2<\begin{matrix}CH(CO_2Et)\cdot CMe\\CH(CO_2Et)—CO\end{matrix}>CH.$$

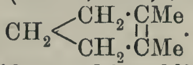
(II.)

Both modifications distil at the same temperature (200°/17 mm.), but do not yield an identical distillate; in each case about 20% of the one being converted into the other. This is the first proof of the existence of two desmotropic forms in a state of vapour.

[With DAVID SPENCE and RICHARD EHRENSTEIN.]—1-Methyl-Δ^1-*cyclo*hexen-3-one-4 : 6-dicarboxylate is obtained as an oil when ethyl 1-methyl*cyclo*hexan-1-ol-3-one-4 : 6-dicarboxylate is allowed to remain for two days in contact with hydrogen chloride in ethereal solution. After several days, crystals of the *enolic* form, m. p. 72°, separate, the residual oil consisting of the *ketonic* form. This has D_4^{20} 1·1687, n_D^{20} 1·4885; it is almost completely transformed into the enolic form by contact with piperidine or tripropylamine. Both modifications give a *sodium* salt, which, however, regenerates the enolic form. The same p-*nitrophenylhydrazone*, m. p. 165°, and *semicarbazone*, m. p. 162—164° (decomp.), were obtained from both the enolic and ketonic tautomerides. J. C. C.

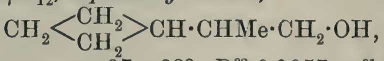
The Action of Aluminium Chloride on Phenyl Mercaptan. J. J. B. DEUSS (*Rec. trav. Chim.*, 1908, **27**, 145—148).—The addition of an excess of aluminium chloride to phenyl mercaptan, dissolved in large excess of light petroleum, results in the formation of diphenyl sulphide and diphenylene disulphide. Hydrogen sulphide is evolved together with a small quantity of hydrogen chloride. W. O. W.

Transformations of *cyclo*Butyldimethylcarbinol. II. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 676—698. Compare Abstr., 1905, i, 772).—The author has examined further the hydrocarbon C_7H_{12}, b. p. 100—102° (*loc. cit.*), and finds it to be identical with Rénard's heptine and with the hydrocarbon obtained by Maquenne from perseitol (Abstr., 1893, i, 635). The constitution of this hydrocarbon is probably



$$CH_2<\begin{matrix}CH_2\cdot CMe\\ \|\\ CH_2\cdot CMe\end{matrix}.$$

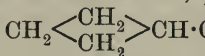
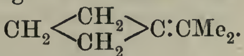
The action of oxalic acid on *cyclo*butyldimethylcarbinol yields, besides the hydrocarbon C_7H_{12}, a *primary alcohol*,



$$CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot CHMe\cdot CH_2\cdot OH,$$

b. p. 157°/773 mm., m. p. 27—28°, D_0^{32} 0·9057, n_D^{31} 1·4489, molecular refraction 33·75 (calc. for cyclic alcohol, 33·74). Its *phenylurethane*, $NHPh\cdot CO\cdot OC_7H_{13}$, crystallises from light petroleum in long needles, m. p. 88—89°, and its *acetate*, $C_7H_{13}\cdot OAc$, has b. p. 171°/751 mm.,

D_0^{15} 0·9403, n_D^{15} 1·4359. On oxidation with potassium dichromate and sulphuric acid, it yields an *aldehyde*, $C_6H_{11}\cdot CHO$, b. p. 144°/751 mm., $D_0^{13\cdot5}$ 0·9072, D_0^{20} 0·8985, $n_D^{13\cdot5}$ 1·4359, which forms a *semicarbazone*, $C_6H_{11}\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2$, m. p. 188—189°, and an *oxime*, $C_6H_{11}\cdot CH{:}NOH$, m. p. 65°. The same aldehyde is obtained on oxidising *cyclo*butyldimethylcarbinol, the oxidation in this case being preceded by transformation into the primary alcohol described above.

The action of hydrobromic acid on this primary alcohol also yields a hydrocarbon, C_7H_{12}, identical with that obtained by the action of oxalic acid on *cyclo*butyldimethylcarbinol. The following are the physical characters of this hydrocarbon, which vary slightly with the source from which it is obtained, probably owing to admixture with the hydrocarbons  $CH_2{<}\substack{CH_2\\CH_2}{>}CH\cdot CMe{:}CH_2$ and  $CH_2{<}\substack{CH_2\\CH_2}{>}C{:}CMe_2$.

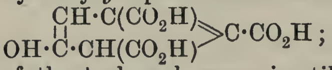
On treatment with concentrated sulphuric acid or hydriodic acid, the hydrocarbon C_7H_{12} is reduced to the compound C_7H_{14} (compare Maquenne, *loc. cit.*), b. p. 94—96°/755—772 mm., D_0^{20} 0·7546—0·7579, n_D^{20} 1·4144. Aschan (*Chemie der alicyklischen Verbindungen*, 473) regards this hydrocarbon C_7H_{14} as possibly identical with 1 : 3-dimethyl*cyclo*pentane, but the author regards it as, more probably, a mixture of 1 : 2-dimethyl*cyclo*pentane with a small proportion of methyl*cyclo*hexane.

The union of hydrogen bromide with the compound C_7H_{12} yields an unstable bromo-derivative, as also does the action of hydrobromic acid on the primary alcohol $C_7H_{13}\cdot OH$. The nitrosochloride, $C_7H_{12}\cdot NOCl$, prepared from the hydrocarbon C_7H_{12}, has m. p. 73—75°, and the dibromide, $C_7H_{12}Br_2$, m. p. 115—115·5°. The hexabromo-derivative, m. p. 134°, was also prepared (compare also Rénard, Abstr., 1887, 565; Maquenne, Abstr., 1889, 32, 361; 1892, 1065; Markownikoff, Abstr., 1904, i, 384).
T. H. P.

Cholesterol. STEFAN MINOVICI (*Ber.*, 1908, **41**, 1561—1565).—A study of the action of sulphuric and hydrochloric acids on cholesterol (compare Mauthner, Abstr., 1906, i, 579). Gradual addition of concentrated hydrochloric acid to cholesterol in boiling alcoholic solution leads to the formation of *cholesteryl ether*, $(C_{27}H_{43})_2O$ or $(C_{27}H_{45})_2O$, which crystallises in yellow needles, m. p. 74·5°, forms a viscid *additive* compound with bromine, gives a yellow, fluorescent coloration with concentrated hydrochloric acid, and is isomeric with Mauthner and Suida's ether (Abstr., 1896, i, 425).

When heated on the water-bath with equal volumes of concentrated sulphuric acid and water, cholesterol yields (*a*) a *cholesteryl ether*, which forms white crystals, m. p. 201°, gives a yellow coloration, and fluorescence with concentrated sulphuric acid, and is considered to be isomeric with the preceding ether and Mauthner and Suida's ether; it forms a *tetrabromide*, $(C_{27}H_{43}Br_2)_2O$ or $(C_{27}H_{45}Br_2)_2O$, crystallising in needles, m. p. 174·5° (decomp.). (*b*) The cholesteryl ether, m. p. 74·5°; and (*c*) a *substance*, which crystallises in spangles, m. p. 135—136°, and appears to form cholesterol on repeated recrystallisation.
G. Y.

Cholesterol, Cholic Acid, and a Common Degradation Product of the Same. Hugo Schrötter, Richard Weitzenböck, and Reinhold Witt (*Monatsh.*, 1908, **29**, 245—254).—Both cholesterol and cholic acid, when heated with concentrated sulphuric acid in the presence of a small quantity of mercury, yield a mixture of acids, which when treated with strong nitric acid yields *rhizocholic acid*, $C_8H_6O_7$, crystallising in small, white needles, m. p. 228—230°; the *silver* salt, $C_8H_3O_7Ag_3$, is a white precipitate; the *barium* and *calcium* salts are more soluble in cold than in hot water.

Since the acid is so stable towards concentrated sulphuric acid and nitric acid, the three carboxylic groups are evidently attached to three different carbon atoms. It is therefore suggested that the acid is a hydroxy*cyclo*pentadienetricarboxylic acid having the composition  $\left.\begin{matrix}\mathrm{CH\cdot C(CO_2H)}\\ \|\\ \mathrm{OH\cdot C\cdot CH(CO_2H)}\end{matrix}\right>\mathrm{C\cdot CO_2H}$; the position of the ethylene linking and of the hydroxyl group is still uncertain. Since this carbon nucleus is characteristic of terpenes and camphenes, it is concluded that not only do cholesterol and cholic acid have a similar structure, but are also connected with the terpenes. W. H. G.

Non-hydrolysable Constituents of Cacao Butter. Hermann Matthes and O. Rohdich (*Ber.*, 1908, **41**, 1591—1592).—The two phytosterols, obtained previously from cacao butter (this vol., i, 199), are best prepared from crude phytosterol acetate; this is brominated in glacial acetic acid solution, and the bromides separated, reduced, and hydrolysed. Phytosterol acetate tetrabromide yields phytosterol, which crystallises in monoclinic leaflets, m. p. 162—163° (stigmasterol, m. p. 146°: *loc. cit.*). Phytosterol acetate dibromide yields phytosterol, which forms doubly refracting, hexagonal crystals, m. p. 139° (135—136°: *loc. cit.*).

Phytosterol and a yellow, unsaturated oil with a pleasant odour are obtained on hydrolysis of the fat extracted from cacao shells by light petroleum. G. Y

Hydrogenation of *cyclo*Butanecarboxylic Acid. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 673—676).—In order to throw light on the formation of a 5-carbon atom ring compound from *cyclo*butyldimethylcarbinol by the action of hydriodic acid (compare Abstr., 1905, i, 772), the author has investigated the action of hydriodic acid (D 1·96) on *cyclo*butanecarboxylic acid. When these compounds are heated together in a sealed tube at 200—210° for nine hours, the products obtained are: (1) a small quantity of a substance, b. p. about 150°, having a hydrocarbon-like odour; (2) *n*-valeric acid, which represents the main product. The hydrogenation of *cyclo*butanecarboxylic acid thus differs from that of *cyclo*butyldimethylcarbinol in that it leads merely to the breaking of the tetramethylene ring at a position adjacent to the carboxyl group with formation of an open-chain compound. T. H. P.

The Six Dinitrobenzoic Acids. H. A. Sirks (*Rec. trav. Chim.*, 1908, **27**, 207—250).—This paper consists chiefly of work already published (compare Abstr., 1907, i, 131). Full details are given of the preparation of the dinitrotoluenes and the corresponding dinitrobenzoic acids. Determinations of the constants of dissociation and esterification disclose the fact that these acids may be divided into two classes. The first includes the two acids in which a nitro-group does not adjoin the carboxyl group; these are only slightly dissociated in solution, and show a comparatively high value for the esterification constant. The four remaining acids, however, are much more highly dissociated, and exhibit correspondingly small values for the esterification constant.

A description and sketch is given of an apparatus suitable for the extraction of large quantities of liquid by means of ether.

W. O. W.

Chloromethyl Sulphate. II. Action on Amino-groups. Josef Houben and Hans R. Arnold (*Ber.*, 1908, **41**, 1565—1580. Compare Abstr., 1907, i, 1000).—The action of water on chloromethyl sulphate, $CH_2Cl\cdot SO_4Me$, was found previously to lead to the formation of methylsulphuric acid, formaldehyde, and hydrogen chloride; from this it appears that the chloromethyl is more reactive than the methyl group. Hence it was to be expected that the employment of chloromethyl sulphate as a methylating agent would lead to the formation of chloromethyl derivatives. This has been realised in the case of the three aminobenzoic acids. Anthranilic acid and chloromethyl sulphate form the methosulphate of chloromethylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NH\cdot CH_2Cl,HMeSO_4$, which readily loses hydrogen chloride, forming the methosulphate of methyleneanthranilic acid, $CO_2H\cdot C_6H_4\cdot N\colon CH_2,HMeSO_4$ (Mehner, Abstr., 1901, i, 470; 1902, i, 676). The methyleneanthranilic acid, when liberated, rapidly polymerises, hence the yield of cyanomethylanthranilic acid formed from it by the action of potassium cyanide and hydrogen chloride is the less the longer the methylene acid has been in the free state. *m*- and *p*-Aminobenzoic acids behave in the same manner as the *o*-amino-acid.

The action of chloromethyl sulphate on methylanthranilic acid leads to the formation of a *substance*, which is probably *methylenebismethyldianthranilic acid*, $CH_2(NMe\cdot C_6H_4\cdot CO_2H)_2$, and must be formed by loss of hydrogen chloride from a mol. of methyl chloromethylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NMe\cdot CH_2Cl$, and a mol. of unchanged methylanthranilic acid, $NHMe\cdot C_6H_4\cdot CO_2H$.

The action of chloromethyl sulphate on ammonia and substituted ammonias has also been studied. Whilst the action of chloromethyl sulphate on ammonia leads to the formation of methylamine hydrochloride, hexamethylenetetramine, and ammonium sulphate, diethylamine yields tetraethylmethylenediamine or, under special conditions, chloromethyldiethylamine. Primary and secondary aromatic amines react similarly, forming derivatives of methylenediamine.

The following substances are new:

Methyleneanthranilic acid, $(CO_2H\cdot C_6H_4\cdot N\colon CH_2)_n$, is obtained as a golden-yellow powder, which darkens at 190°, m. p. 210°, is soluble in acids or alkalis, and yields a green *copper*, white *ferrous*, and dark brown *ferric* salt. When treated with concentrated alcoholic hydrogen chloride, the acid yields an unstable *product*, which may be its hydrochloride or chloromethylanthranilic acid.

Chloromethyl sulphate and methyl anthranilate yield a *substance*, which is probably the methyl ester of the polymeric methyleneanthranilic acid, and on reduction with zinc and hydrochloric acid forms polymeric methyleneanthranilic acid together with traces of methylanthranilic acid.

p-*Methyleneaminobenzoic acid*, $(C_8H_7O_2N)_n$. is obtained as a white precipitate, darkening at 220°, decomp. 250°, and absorbs hydrogen chloride, forming a brown, deliquescent *acid*, which may be *p*-chloromethylaminobenzoic acid. p-*Cyanomethylaminobenzoic acid*,

$$CN{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H,$$

prepared together with a small amount of a *substance*, crystallising in white needles, m. p. 225°, from *p*-aminobenzoic acid, formaldehyde, and hydrogen cyanide, or in small amounts by adding potassium cyanide to *p*-methyleneaminobenzoic acid dissolved in dilute hydrochloric acid, forms a white, crystalline powder, m. p. 177° (decomp.).

m-*Methyleneaminobenzoic acid*, $(C_8H_7O_2N)_n$, is obtained as a yellowish-brown powder, decomp. 260°, which absorbs hydrogen chloride, forming an unstable, reddish-brown *product*.

m-*Cyanomethylaminobenzoic acid*, $C_9H_8O_2N_2$, prepared from *m*-aminobenzoic acid, crystallises in yellowish-brown leaflets, m. p. 193°. The product, obtained in small amount by the action of potassium cyanide and hydrochloric acid on *m*-methyleneaminobenzoic acid, has m. p. 182°.

Chloromethyldiethylamine, $NEt_2{\cdot}CH_2Cl$, prepared by the action of chloromethyl sulphate on diethylamine at low temperatures, is unstable and can be isolated only as the *platinichloride*,

$$C_{10}H_{26}N_2Cl_8Pt.$$

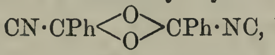
Tetraphenylmethylenediamine, $C_{25}H_{22}N_2$, prepared from chloromethyl sulphate and diphenylamine, forms an unstable, white, crystalline mass, m. p. 82—85°, is soluble in concentrated acids, and gives with nitrous acid a green oil dissolving to a bluish-green solution in ether.

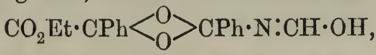
s-*Diphenyldiethylmethylenediamine*, $CH_2(NPhEt)_2$, prepared from ethylaniline, crystallises from acetone in leaflets, m. p. 145°.

Di-p-*bromo*-s-*diphenylmethylenediamine*, $CH_2(NH{\cdot}C_6H_4Br)_2$, from *p*-bromo aniline, crystallises in white leaflets, m. p. 181° (decomp.); the sulphate, $C_{13}H_{14}N_2Br_2,SO_4$, rhombic plates.

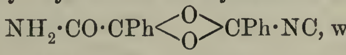
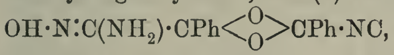
The *di*-m-*bromo* compound forms leaflets, m. p. 135°. 2 : 2′-*Dinitro*-s-*di*-p-*tolylmethylenediamine* $CH_2(NH{\cdot}C_6H_3Me{\cdot}NO_2)_2$, from 2-nitro-*p*-toluidine, crystallises in brown needles, m. p. 207°; the sulphate forms yellowish-white needles. These derivatives of methylenediamine, when heated with sulphuric acid, yield formaldehyde and the corresponding amines. G. Y.

Separation of Hippuric Acid from Urine. HERBERT E. ROAF (*Bio.-Chem. J.*, 1908, 3, 185—187).—To each litre of herbivorous urine, 250 grams of ammonium sulphate and 15 c.c. of concentrated sulphuric acid are added. The hippuric acid then crystallises out readily, and with a comparatively small amount of adherent urinary pigment. This can be removed by recrystallisation after boiling with animal charcoal. W. D. H.

Bisbenzoyl Cyanide. OTTO DIELS and ALBERT PILLOW (*Ber.*, 1908, 41, 1893—1901).—A substance having the composition of benzoyl cyanide, but not identical with it or with trisbenzoyl cyanide, which was obtained by Wache (Abstr., 1889, 681) by the action of sodium on benzoyl cyanide, and by Claisen (Abstr., 1898, i, 423) by treating benzoyl chloride with hydrogen cyanide in presence of pyridine, is now found to be bisbenzoyl cyanide. It is considered to have the constitution  $\mathrm{CN{\cdot}CPh}{<}\substack{\mathrm{O}\\\mathrm{O}}{>}\mathrm{CPh{\cdot}NC}$, because (1) it does not give ketone reactions. (2) When treated with alcoholic hydrogen chloride, it forms an additive compound with 1 mol. of water, whilst at the same time one cyanogen group is converted into a carbethoxy-group; the resulting *ester*, which is formulated as



$$\mathrm{CO_2Et{\cdot}CPh}{<}\substack{\mathrm{O}\\\mathrm{O}}{>}\mathrm{CPh{\cdot}N{:}CH{\cdot}OH},$$

crystallises in prisms, m. p. 143—144°, forms with phenylcarbimide an *additive* compound, $C_{25}H_{22}O_6N_2$, crystallising in short prisms, m. p. 163—164°, and when treated with alkalis is hydrolysed, yielding benzoylformic acid, benzamide, formic acid, and ethyl alcohol. (3) Treatment of bisbenzoyl cyanide with hydriodic acid leads to the formation of an *amide*,  $\mathrm{NH_2{\cdot}CO{\cdot}CPh}{<}\substack{\mathrm{O}\\\mathrm{O}}{>}\mathrm{CPh{\cdot}NC}$, which crystallises in rhombic prisms, m. p. 174—177° (decomp.), cannot be converted into the preceding ester by treatment with alcoholic hydrogen chloride, and is hydrolysed by alkalis, yielding benzoylformamide, benzoic acid, and hydrogen cyanide; and (4) bisbenzoyl cyanide forms an *amidoxime*,  $\mathrm{OH{\cdot}N{:}C(NH_2){\cdot}CPh}{<}\substack{\mathrm{O}\\\mathrm{O}}{>}\mathrm{CPh{\cdot}NC}$, which crystallises in rectangular prisms, m. p. 181° (decomp.), and on hydrolysis yields benzoic acid, hydrogen cyanide, and *benzoylformamidoxime*, $\mathrm{COPh{\cdot}C(NH_2){:}N{\cdot}OH}$, crystallising in quadratic prisms, m. p. 133—134°. When treated successively with phosphorus pentachloride in ethereal solution and with ice, this undergoes Beckmann's transformation, yielding benzoylcarbamide. G. Y.

Synthesis of Polypeptides. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Ber.*, 1908, 41, 1991).—In the paper XV on the derivatives of 2 : 5-di-iodo-*l*-tyrosine (this vol., i, 420), the figures should be 3 : 5 in place of 2 : 5 throughout. C. S.

Liberation of Carbon Monoxide from Secondary and Primary Carboxylic Acids. AUGUSTIN BISTRZYCKI and B. VON SIEMIRADZKI (*Ber.*, 1908, 41, 1665—1672. Compare Oechsner de Coninck and Raynaud, Abstr., 1903, i, 457, 458).—In continuation of the work previously published (Abstr., 1906, i, 135), the liberation of carbon monoxide from various secondary and primary carboxylic acids when heated with concentrated sulphuric acid has been investigated. Most of the secondary acids studied, when heated with sulphuric acid, evolve roughly two-thirds to three-quarters of the theoretical amount of carbon monoxide, whilst the primary acids yield relatively far less carbon monoxide. As a rule, the stability of the normal primary acids decreases with an increase in the number of methylene groups, whilst the normal acids are more stable than their isomerides with side-chains.

The secondary acids investigated were diphenylacetic acid, tetranitrodiphenylacetic acid, dibromo-*p*-hydroxydiphenylacetic acid,

$$C_6H_2Br_2(OH)\cdot CHPh\cdot CO_2H,$$

2 : 5-dimethylhydratropic acid, $C_6H_3Me_2\cdot CHMe\cdot CO_2H$, hexahydrobenzoic acid, quinic acid, and sulphocamphylic acid. The last acid is very stable towards sulphuric acid; when camphoric acid is heated with sulphuric acid at 200°, only slightly more than 1 mol. of carbon monoxide is evolved from 1 mol. of the acid, showing that the introduction of a sulphonic group into the acid radicle prevents the evolution of carbon monoxide. The primary acids studied were butyric acid, *iso*butyric acid, α-ethylbutyric acid, valeric acid, *iso*valeric acid, hexoic acid, and γ-methylvaleric acid. W. H. G.

Action of Ammonia and Amines on Cinnamenylacrylic [Cinnamylideneacetic] Acid and its Methyl Ester. ADOLF RIEDEL (*Annalen*, 1908, **361**, 96—108).—Hinrichsen observed (Abstr., 1904, i, 1012) that cinnamylideneacetic acid and its salts do not react with phosphorus pentachloride. This is in agreement with Meyer's observation (Abstr., 1901, i, 407) that acids with conjugated double linkings, if containing a second negative group in the δ-position to the carboxyl, are, in general, incapable of forming acid chlorides. The present author has found that methyl cinnamylideneacetate does not react with phosphorus pentachloride, but has obtained the amide in about an 8% yield by heating the methyl ester with alcoholic ammonia at 140—160°. Primary aliphatic amines, and to a very small extent secondary amines, such as diethylamine and piperidine, react with methyl cinnamylideneacetate in the same manner as does ammonia. Primary aromatic amines, on the other hand, do not react with the ester when boiled in a reflux apparatus, whilst at higher temperatures complete decomposition takes place. When heated with cinnamylideneacetic acid, aniline and *o*-toluidine form salts.

Cinnamylideneacetamide, $CHPh⁚CH\cdot CH⁚CH\cdot CO\cdot NH_2$, crystallises in yellow leaflets, m. p. 185°, decolorises bromine and permanganate solutions, and when heated with acetic anhydride in benzene solution yields the *acetyl* derivative, $CHPh⁚CH\cdot CH⁚CH\cdot CO\cdot NHAc$, crystallising in yellow leaflets, m. p. 177—178°. The *methylamide*,

$$CHPh⁚CH\cdot CH⁚CH\cdot CO\cdot NHMe,$$

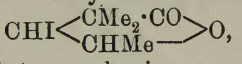
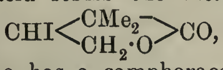
crystallises in white needles, m. p. 157°; the *ethylamide*, $C_{13}H_{15}ON$, white needles, m. p. 143—144°; the *propylamide*, $C_{14}H_{17}ON$, white needles, m. p. 133°; the *butylamide*, $C_{15}H_{19}ON$, white crystals, m. p. 119—120°; the *diethylamide*, $C_{15}H_{19}ON$, white crystals, m. p. 106°; the *piperidide*, $CHPh⁚CH\cdot CH⁚CH\cdot CO\cdot NC_5H_{10}$, colourless leaflets, m. p. 203° (decomp.).

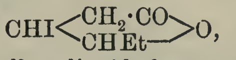
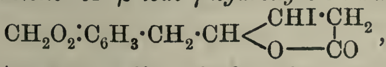
The cinnamylideneacetates of the following bases are described; the temperatures are melting points. Methylamine, white needles, 142—143°; ethylamine, white leaflets, 117—118°; propylamine, white leaflets, 140° (decomp.); butylamine, white leaflets, 107—108°; aniline, greenish-white needles, 184°; *o*-toluidine, reddish-white needles; diethylamine, crystalline varnish, 80°; piperidine, white prisms, 111°; guanidine, yellowish-white leaflets, 220°. G. Y.

3 : 5-Dinitro-4-hydroxybenzoic Acid. FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1908, [iv], **3**, 591—593; *Arch. sci. phys. nat.*, 1908, **25**, 474—478).—This acid, first prepared by Barth (*Zeit. Chem.*, 1866, 647) by nitration of *p*-hydroxybenzoic acid, was subsequently obtained by Salkowski from chrysanisic acid (Abstr., 1872, 555), but the latter investigator expressed doubt as to the identity of the two acids. The results of the present work, undertaken to decide this point, show that the two are identical.

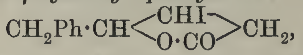
p-Hydroxybenzoic acid, nitrated by Barth's method, yields in addition to 3 : 5-dinitro-4-hydroxybenzoic acid, 3-nitro-4-hydroxybenzoic acid and 2 : 4-dinitrophenol. The ethyl ester of the dinitro-acid can be obtained by direct nitration of ethyl *p*-hydroxybenzoate. The *methyl* ester, m. p. 115—116°, similarly obtained, crystallises in colourless, prismatic needles, and is readily hydrolysed by ebullition with sodium carbonate solution. The dinitro-acid itself is best obtained by nitrating *p*-hydroxybenzoic acid dissolved in sulphuric acid and kept at 0°, with a mixture of equal parts of sulphuric acid and nitric acid (D 1·52). 3 : 5-*Diamino-4-hydroxybenzoic acid*, m. p. 205°, obtained by reducing the dinitro-acid with tin and hydrochloric acid, is readily oxidisable. The *hydrochloride* and *sulphate* are crystalline. T. A. H.

Action of Nascent Hypoiodous Acid on Unsaturated Acids. Iodo-lactones. J. BOUGAULT (*Ann. Chim. Phys.*, 1908, [viii], **14**, 145—183).—The first part of the paper contains an epitome of previous work (compare Abstr., 1905, i, 9; 1906, i, 848; 1908, i, 179, 269). A number of new iodo-lactones are described; these have been obtained by the action of mercuric oxide and iodine on $\beta\gamma$- or $\gamma\delta$-unsaturated acids.

$\alpha\alpha$-Dimethyl-Δ^{β}-pentenoic acid yields the *lactone* of *β-iodo-γ-hydroxy-αα-dimethylvaleric acid*,  $\mathrm{CHI}<^{\mathrm{CMe_2\cdot CO}}_{\mathrm{CHMe}\text{—}}>\mathrm{O}$, m. p. 86°, a colourless, crystalline, neutral substance having a camphoraceous odour. $\alpha\alpha$-Dimethyl*iso*crotonic acid forms the *lactone* of *β-iodo-γ-hydroxy-αα-dimethylbutyryic acid*,  $\mathrm{CHI}<^{\mathrm{CMe_2}\text{—}}_{\mathrm{CH_2\cdot O}}>\mathrm{CO}$, a yellow liquid, which, like the preceding lactone, has a camphoraceous odour and is decomposed on boiling with aqueous sodium hydroxide.

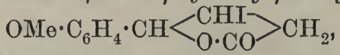
The *lactone* of *β-iodo-γ-hydroxyhexoic acid*,  $\mathrm{CHI}<^{\mathrm{CH_2\cdot CO}}_{\mathrm{CHEt}\text{—}}>\mathrm{O}$, prepared from Δ^{α}-hydrosorbic acid, is a thick, yellow liquid, decomposing when distilled under atmospheric pressure. Fittig's α-hydropiperic acid furnishes the *lactone* of *β-iodo-γ-hydroxy-δ-3 : 4-methylenedioxyphenylvaleric acid*,  $\mathrm{CH_2O_2{:}C_6H_3\cdot CH_2\cdot CH}<^{\mathrm{CHI\cdot CH_2}}_{\mathrm{O}\text{——}\mathrm{CO}}$, yellow crystals, m. p. 104°. Aqueous sodium hydroxide converts this into the γ-ketonic acid, $\mathrm{CH_2O_2{:}C_6H_3\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H}$, whilst ammonium sulphite transforms it into the ammonium salt of a new sulphonic acid, $\mathrm{CH_2O_2{:}C_6H_3\cdot CH_2\cdot CH}<\genfrac{}{}{0pt}{}{\mathrm{CH(SO_3NH_4)}}{\mathrm{O\text{———}-CO}}>\mathrm{CH_2}$, which crystallises from hot water in glistening plates. The corresponding *barium* salt crystallises with $2H_2O$, and, when oxidised by potassium permanganate, furnishes piperonylic acid, homopiperonylic acid, and methylenedioxyphenylglyoxylic acid.

The *lactone* of *β-iodo-γ-hydroxy-δ-phenylvaleric acid*,



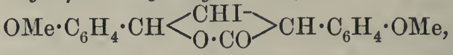
$$\mathrm{CH_2Ph\cdot CH}<\genfrac{}{}{0pt}{}{\mathrm{CHI-}}{\mathrm{O\cdot CO}}>\mathrm{CH_2},$$

forms yellow crystals, m. p. 83°, and is prepared from hydrocinnamylideneacetic acid. Sodium hydroxide transforms it into the corresponding γ-ketonic acid, and in its behaviour with ammonium sulphite it resembles the preceding lactone. The *barium* salt has the composition $\mathrm{(C_{11}H_{11}O_2SO_3)_2Ba,3H_2O}$. Phenyl*iso*crotonic acid is the starting point for the preparation of the *lactone* of *β-iodo-γ-hydroxy-γ-phenylbutyric acid*, $\mathrm{CHPh}<\genfrac{}{}{0pt}{}{\mathrm{CHI-}}{\mathrm{O\cdot CO}}>\mathrm{CH_2}$, m. p. 116°. This compound differs from the two foregoing lactones in its behaviour towards sodium hydroxide and ammonium sulphite. The *lactone* of *β-iodo-γ-hydroxy-αδ-diphenylvaleric acid*, $\mathrm{CH_2Ph\cdot CH}<\genfrac{}{}{0pt}{}{\mathrm{CHI-}}{\mathrm{O\cdot CO}}>\mathrm{CHPh}$, yellow crystals, m. p. 106°, is obtained from Rebuffat's hydrophenylcinnamylidene acetic acid. The *lactone* of *β-iodo-γ-hydroxy-γ-anisylvaleric acid*,



$$\mathrm{OMe\cdot C_6H_4\cdot CH}<\genfrac{}{}{0pt}{}{\mathrm{CHI-}}{\mathrm{O\cdot CO}}>\mathrm{CH_2},$$

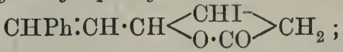
m. p. 125°, is prepared from anisyl*iso*crotonic acid. The *lactone* of *β-iodo-γ-hydroxy-αγ-dianisylbutyric acid*,



$$\mathrm{OMe\cdot C_6H_4\cdot CH}<\genfrac{}{}{0pt}{}{\mathrm{CHI-}}{\mathrm{O\cdot CO}}>\mathrm{CH\cdot C_6H_4\cdot OMe},$$

yellow crystals, m. p. 115°, is obtained from Fittig's dianisylpentenoic acid.

The two following iodo-lactones are obtained from unsaturated acids of the general formula $\mathrm{CHR{:}CH\cdot CH_2\cdot CH_2\cdot CO_2H}$. The *lactone* of *γ-iodo-δ-hydroxyvaleric acid*, $\mathrm{CHI}<\genfrac{}{}{0pt}{}{\mathrm{CH_2\cdot CH_2}}{\mathrm{CH_2\text{——}O}}>\mathrm{CO}$, is a liquid, becoming brown on exposure and decomposing when distilled. The *lactone* of *γ-iodo-δ-hydroxy-δ-phenylvaleric acid*, $\mathrm{CHI}<\genfrac{}{}{0pt}{}{\mathrm{CH_2\cdot CH_2}}{\mathrm{CHPh\cdot O-}}>\mathrm{CO}$, forms yellow crystals, m. p. 90°. Cinnamenyl*iso*crotonic acid yields the *lactone* of *β-iodo-γ-hydroxy-ε-phenyl-Δ^δ-hexenoic acid*,

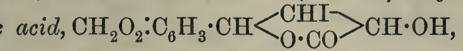


$$\mathrm{CHPh{:}CH\cdot CH}<\genfrac{}{}{0pt}{}{\mathrm{CHI-}}{\mathrm{O\cdot CO}}>\mathrm{CH_2}\,;$$

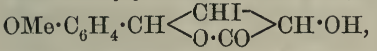
this is sparingly soluble in alcohol and has m. p. 125°.

Anisylpyruvic acid, on partial reduction with sodium amalgam, gives α-hydroxy-γ-phenyl*iso*crotonic acid, $\mathrm{CHPh\cdot CH{:}CH\cdot CH(OH)\cdot CO_2H}$. This was not isolated, but on treating an aqueous solution of its sodium salt with iodine the *lactone* of *β-iodo-αγ-dihydroxy-γ-phenylbutyric acid*, $\mathrm{CHI}<\genfrac{}{}{0pt}{}{\mathrm{CH(OH)}}{\mathrm{CHPh\cdot O}}>\mathrm{CO}$, was formed. This occurs as yellow crystals, which darken at 125° and melt with decomposition at 132°. It is much more soluble in the ordinary media than the preceding lactones. Similarly, *α-hydroxy-γ-piperonyl*iso*crotonic acid*,

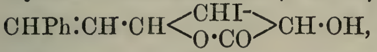
$$CH_2O_2:C_6H_3\cdot CH:CH\cdot CH(OH)\cdot CO_2H,$$

m. p. 143°, furnishes the *lactone* of *β-iodo-αγ-dihydroxy-γ-methylenedioxybutyric acid*,  $CH_2O_2:C_6H_3\cdot CH<\substack{CHI-\\O\cdot CO}>CH\cdot OH$, small, yellow needles, m. p. 150°. When anisylidenepyruvic acid is partly reduced by sodium amalgam, *α-hydroxy-γ-anisyl*iso*crotonic acid*,

$$OMe\cdot C_6H_4\cdot CH:CH\cdot CH(OH)\cdot CO_2H,$$

m. p. 145°, is obtained together with *α-hydroxy-γ-anisylbutyric acid*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CO_2H$, m. p. 116—117°. The former acid readily yields the *lactone* of *β-iodo-αγ-dihydroxy-γ-anisylbutyric acid*,  $OMe\cdot C_6H_4\cdot CH<\substack{CHI-\\O\cdot CO}>CH\cdot OH$, m. p. 122°. Cinnamylidenepyruvic acid can be reduced to *α-hydroxy-γ-cinnamenyl*iso*crotonic acid*,

$$CHPh:CH\cdot CH:CH\cdot CH(OH)\cdot CO_2H,$$

the sodium salt of which reacts readily with iodine to form yellow crystals of the *lactone* of *β-iodo-αγ-dihydroxy-ε-phenyl-Δ$^{\delta}$-hexenoic acid*,  $CHPh:CH\cdot CH<\substack{CHI-\\O\cdot CO}>CH\cdot OH$, m. p. 122°.

The following βγ-unsaturated acids having a ketonic group in the α-position cannot be made to yield iodo-lactones: *piperonylidenepyruvic acid*, $CH_2O_2:C_6H_3\cdot CH:CH\cdot CO\cdot CO_2H$, m. p. 161°; *anisylidenepyruvic acid*, $OMe\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CO_2H$, m. p. 131°; *furfurylidenepyruvic acid*, $C_4H_4O\cdot CH:CH\cdot CO\cdot CO_2H$, m. p. 111°; p-*methoxyhydratropylidenepyruvic acid*, $OMe\cdot C_6H_4\cdot CHMe\cdot CH:CH\cdot CO\cdot CO_2H$, m. p. 180°.

W. O. W.

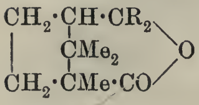
Nitrobenzoylbenzoic Acids. J. Rainer (*Monatsh.*, 1908, **29**, 177—180).—The compound obtained by Lang (Abstr., 1905, i, 895) by adding *o*-benzoylbenzoic acid to nitric acid (1·52), and described as being identical with Kliegl's *p*-nitro-*o*-benzoylbenzoic acid (Abstr., 1905, i, 187), is shown to be 3′-nitro-*o*-benzoylbenzoic acid,

$$NO_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO_2H$$

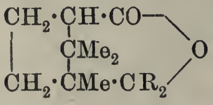
(compare Basler Chemische Fabrik, Abstr., 1904, i, 512). A compound was obtained in the preparation of *p*-nitro-*o*-benzoylbenzoic acid by Kliegl's method which is probably m-*nitro*-o-*benzoylbenzoic acid*, $COPh\cdot C_6H_3(NO_2)\cdot CO_2H$; it crystallises in rectangular leaflets, m. p. 212°.

W. H. G.

Reactions of Dicarboxylic Anhydrides with Magnesium Organic Compounds. Josef Houben and Arnold Hahn (*Ber.*, 1908, **41**, 1580—1588).—The authors have studied the action of magnesium organic compounds on camphoric anhydride. As this reaction takes place less simply (Komppa, this vol., i, 352) than that with the anhydrides of monocarboxylic acids or with phthalic anhydride, the study has been extended to other dicarboxylic anhydrides. It is found that, whilst phthalic, naphthalic, camphoric, and citraconic anhydrides react readily, the last with almost explosive violence, with magnesium organic compounds, succinic anhydride reacts with great difficulty, and to an almost complete extent only in boiling toluene solution. With succinic anhydride, the reaction leads to the formation of products, $C_2H_4(CR_2\cdot OH)_2$, in which the two carbonyl oxygen atoms are displaced each by two alkyl groups. Thus succinic anhydride and magnesium phenyl bromide yield tetraphenylbutandiol, m. p. 205—206° (Dilthey and Last, Abstr., 1904, i, 667). Camphoric anhydride, on the other hand, forms isomeric campholides (annexed formulæ), two alkyl groups being substituted for only one of the two carbonyl oxygen atoms.

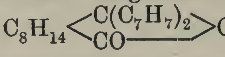


and



αaδδ-Tetrabenzylbutan-αδ-diol, $OH{\cdot}C(C_7H_7)_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(C_7H_7)_2{\cdot}OH$, prepared from succinic anhydride and magnesium benzyl chloride, crystallises in needles, m. p. 129°, and gives a red coloration with concentrated sulphuric acid. The by-products of the reaction are probably unsaturated hydrocarbons or benzylated hydrofurans.

The action of magnesium ethyl bromide on succinic anhydride leads to the formation of *tetraethylhydrofuran*, $C_{12}H_{24}O$, which is obtained as an oil, b. p. about 80—120°/11 mm.

Camphoric anhydride and magnesium benzyl chloride form two dibenzylcampholides,  $C_8H_{14}{<}\begin{matrix}C(C_7H_7)_2\\CO\end{matrix}{>}O$, which are separated by means of the sodium salts of the corresponding hydroxycampholic acids.

a-*Dibenzylhydroxycampholic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}C(C_7H_7)_2{\cdot}OH$, crystallises in needles containing alcohol of crystallisation, m. p. 177—178°, and is electrified when dried and rubbed. The *sodium* salt is sparingly soluble; the *barium* salt was analysed. a-*Dibenzylcampholide* is best prepared by boiling the acid with acetyl chloride, or by distillation of the acid in a vacuum; it forms prisms, m. p. 118°.

b-*Dibenzylhydroxycampholic acid* crystallises in needles, m. p. 145°. b-*Dibenzylcampholide* crystallises in needles, m. p. 114°. A mixture of the two dibenzylcampholides has m. p. about 50°. The allocation of the two constitutions requires further investigation. G. Y.

Preparation of Benzilic Acid. Hans von Liebig (*Ber.*, 1908, 41, 1644—1645).—A 90—95% yield of this acid, free from benzoic acid, and therefore much better than that ordinarily obtained, results when 100 grams of benzil are boiled with a 50% aqueous solution of 100 grams of potassium hydroxide and 200 grams of alcohol for ten to twelve minutes; the mass is then left for several hours before collecting the salt, which is well washed with alcohol, then dissolved in cold water, heated to boiling, and the benzilic acid precipitated with sulphuric acid. W. R.

Tritancarboxylic Acids. Hans von Liebig (*Ber.*, 1908, 41, 1645—1648. Compare Abstr., 1905, i, 781; 1907, i, 45, 930—1045; this vol., i, 445).—Cooled sulphuric acid gives in the condensation of benzil with hydroxybenzenes fairly good yields of *p*-hydroxytritanic acids, but poor yields of the ortho-acids. In order to obtain these acids in better yields, benzilic acid has been substituted, and experiments carried out by heating the molten acid with the phenol, the fusion treated twice with boiling water and then twice with 5% sodium carbonate to remove the free hydroxytritanic acid; the residue consists of lactone.

Resorcinol gives an almost quantitative yield of 2 : 4-dihydroxytritanolactone (1905, *loc. cit.*), and phenol an 80—90% yield of *p*-hydroxytritanic acid (Bistrzycki and Nowakowski, Abstr., 1901, i, 716) and 10—20% of *o*-hydroxytritanolactone (1907, *loc. cit.*).

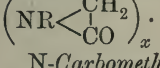
o-Cresol leads to the formation of *2-hydroxy-3-methyltritanolactone*, $C_{21}H_{16}O_2$, which crystallises from alcohol in stout needles, m. p. 136—137°, and *4-phenoxy-3-methyltritanic acid*, which sinters at 130°, froths at 140—143°, and is thereby converted into the *anhydride*, $C_{42}H_{34}O_5$, m. p. 215°. *m*-Cresol gives 4-hydroxy-2-methyltritanic acid and 2-hydroxy-4-methyltritanolactone (Bistrzycki and Nowakowski, *loc. cit.*). *p*-Cresol, in addition to the lactone (m. p. 132° : Bistrzycki gives 130°) and the *p*-acid, gives the 5 : 5′-*ether* of 4 : 4′-*dihydroxy*-2 : 2′-*dimethyltritanic acid*, $C_{42}H_{34}O_5$, which crystallises from benzene in needles, m. p. 245°.

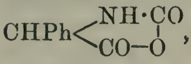
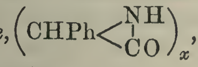
Thymol yields the *p*-hydroxy-acid (Geipert, Abstr., 1904, i, 319) and a small quantity of 2-*hydroxy*-3-*methyl*-6-iso*propyltritanolactone*, crystallising in leaflets, m. p. 124°. Quinol gives 2 : 5-dihydroxytritanolactone (m. p. 200—201° : Tarczynsky, *Diss.*, Freiburg, gives 194°). *Methyl* 2 : 5-*dimethoxytritanate*, $C_{23}H_{22}O_4$, crystallises in glistening leaflets from alcohol, m. p. 133°. Catechol gives 2 : 3-*dihydroxytritanolactone*, which separates from alcohol in fine crystals, m. p. 136°.

Guaiacol gives a mixture, one constituent of which is probably 4-*hydroxy*-3-*methoxytritanic acid*, $C_{21}H_{18}O_4$, crystals, m. p. 194°. Orcinol leads to the formation of 2 : 4-*dihydroxy*-6-*methyltritanolactone*, $C_{21}H_{16}O_3$, the crystals of which contain benzene of crystallisation, m. p. 177°, after warming, and pyrogallol yields 2 : 3 : 4-*trihydroxytritanolactone*, $C_{20}H_{14}O_3$, large crystals from benzene, m. p. 184°.

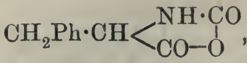
W. R.

Anhydrides of α-Amino-*N*-carboxylic Acids and of α-Amino-acids. Hermann Leuchs and Walter Geiger (*Ber.*, 1908, 41, 1721—1726. Compare Abstr., 1906, i, 236; 1907, i, 770).

—Anhydrides have been obtained by the action of thionyl chloride on the carbomethoxy-derivatives of *C*-phenylaminoacetic acid, phenylalanine, and leucine. The anhydrides crystallise well, and have low melting points. They are readily decomposed by water or absolute alcohol, yielding carbon dioxide and amorphous compounds of the type  $\left(NR<\begin{matrix}CH_2\\|\\CO\end{matrix}\right)_x$.

N-*Carbomethoxy*-C-*phenylglycine*, $CO_2Me\cdot NH\cdot CHPh\cdot CO_2H$, crystallises from water or benzene in needles, m. p. 87—88°. The *anhydride*,  $CHPh<\begin{matrix}NH\cdot CO\\ \quad\ \ |\\CO-O\end{matrix}$, crystallises from benzene or chloroform in prisms, m. p. 99—100° (decomp.), and when boiled with absolute alcohol, yields *phenylglycine anhydride*,  $\left(CHPh<\begin{matrix}NH\\|\\CO\end{matrix}\right)_x$, as an amorphous powder insoluble in all ordinary solvents.

N-*Carbomethoxyphenylalanine*, $CH_2Ph\cdot CH(CO_2H)\cdot NH\cdot CO_2Me$, is a syrup, and the corresponding *phenylalanine*-N-*carboxylic anhydride*,


$\mathrm{CH_2Ph\cdot CH}<\begin{array}{l}\mathrm{NH\cdot CO}\\ \qquad\;\;|\\ \mathrm{CO{-}O}\end{array}$, crystallises from cold ethyl acetate in colourless, glistening, rectangular plates, m. p. 127—128°.

N-*Carbomethoxyleucine* is a viscid oil, and *leucine*-N-*carboxylic anhydride*, $C_7H_{11}O_3N$, crystallises from benzene in colourless prisms, m. p. 48—50°. At above 80°, it loses carbon dioxide. J. J. S.

Amide Acids of Phenylsuccinic Acid. RICHARD ANSCHÜTZ and PAUL WALTER (*Annalen*, 1908, **361**, 73—78).—It was found previously (Abstr., 1907, i, 766) that the action of ammonia or of substituted ammonias on phenylsuccinic anhydride leads to the formation of phenylsuccin-β-amic acids, $CO_2H\cdot CHPh\cdot CH_2\cdot CO\cdot NHR$, the basic group combining with the carbonyl of the more feebly acid carboxyl. Lüttgen, on the other hand, on treating phenylsuccinic anhydride with ammonia, converting the resulting acid into the silver salt, and heating this with ethyl iodide, obtained small amounts of β-ethyl phenylsuccin-α-amate, $NH_2\cdot CO\cdot CHPh\cdot CH_2\cdot CO_2Et$, which he prepared also by the action of potassium cyanide on ethyl benzylidenemalonate and distillation of the resulting ethyl hydrogen β-carbamylbenzylmalonate, $NH_2\cdot CO\cdot CHPh\cdot CH(CO_2Et)\cdot CO_2H$ (*Diss.*, Bonn, 1899). The comparison of these results made it appear probable that the action of ammonia on phenylsuccinic anhydride leads to the formation of a mixture of phenylsuccinamic acids, the β-amic acid being the chief product, and that Lüttgen's esterification product was a mixture of esters, from which he isolated only the more sparingly soluble isomeride. These views have now been confirmed.

β-Ethyl phenylsuccin-α-amate, prepared by the action of concentrated sulphuric acid on ethyl β-cyano-β-phenylpropionate, has m. p. 173° (167°: Lüttgen, *loc. cit.*).

When converted into the silver salt and heated with ethyl iodide at 50—60°, the product of the action of ammonia on phenylsuccinic anhydride yields chiefly α-ethyl phenylsuccin-β-amate together with small amounts of the β-ethyl α-amate. By converting the mixed amic acids into the corresponding methyl esters, which can be readily separated quantitatively, it is shown that only about 5% of the reaction product is the α-amic acid, the reaction of the anhydride with ammonia taking place to the extent of 95% according to the rule previously laid down. G. Y.

Wandering of Alkyl Groups During the Distillation of Ether Acids. JACQUES POLLAK and H. FELDSCHAREK (*Monatsh.*, 1908, **29**, 139—155).—Nitro-2 : 3 : 4-trimethoxybenzoic acid when distilled was found by Pollak and Goldstein (Abstr., 1907, i, 320) to be converted into the methyl ester of the acid. The object of this investigation was to ascertain whether the esterification of the acid depends on the presence of the nitro-group, and to what extent the change is influenced by the number and positions of the methoxy- and nitro-groups. The following substances were distilled under the ordinary and under reduced pressure: nitro-3 : 4 : 5-trimethoxybenzoic acid, dinitroanisic acid, nitroanisic acid, 3 : 4 : 5-trimethoxybenzoic acid, *o*-methoxybenzoic acid, *m*-methoxybenzoic acid, and anisic acid. The results obtained may be summarised as follows: (1) The presence of a nitro-group in the molecule decreases the stability of the acid and favours the formation of the ester; thus, nitro-3 : 4 : 5-trimethoxybenzoic acid and dinitroanisic acid are largely converted into their methyl esters when distilled in a vacuum. (2) An increase in the number of nitro-groups is accompanied by a marked decrease in stability; thus, dinitroanisic acid decomposes with the formation of the methyl ester when distilled under a pressure of 12 mm., whilst nitroanisic acid is only partly converted into its ester when slowly distilled under a pressure of 40 mm. (3) The methoxy-acids which do not contain a nitro-group may be distilled in a vacuum without undergoing decomposition. *o*-Methoxybenzoic acid, when distilled under the ordinary pressure, decomposes, yielding a mixture of methyl salicylate and methyl *o*-methoxybenzoate. Anisic acid and, more especially, *m*-methoxybenzoic acid are far more stable than the ortho-compound. However, the methyl esters of these acids are also formed on heating them for several hours at 180—270°. (4) Since *o*-methoxybenzoic acid decomposes far more readily than 3 : 4 : 5-trimethoxybenzoic acid, it follows that the ortho-position of the groups has a greater influence on the stability of the compound than the presence of a large number of methoxy-groups not ortho to the carboxyl group. 3 : 4 : 5-Trimethoxybenzoic acid is, however, far less stable than either anisic or *m*-methoxybenzoic acid.

Ethyl 3 : 4 : 5-*trimethoxybenzoate*, $C_6H_2(OMe)_3\cdot CO_2Et$, prepared by the action of methyl sulphate and potassium hydroxide on ethyl gallate, crystallises in white leaflets, m. p. 53—57°; the *nitro*-derivative, $NO_2\cdot C_6H(OMe)_3\cdot CO_2Et$, forms yellow crystals, m. p. 68—70°, and yields, on hydrolysis, the *acid*, $NO_2\cdot C_6H(OMe)_3\cdot CO_2H$, m. p. 164°.

W. H. G.

Santoninic Acid. ANGELO ANGELI and LUIGI MARINO (*Mem. R. Accad. Lincei*, 1908, [v], 6, 385—401. Compare Abstr., 1907, i, 321).—The following oxidation products of santonin have been obtained by the authors.

Dioxysantonin, $C_{15}H_{18}O_5$, obtained by oxidising santonin in sodium hydroxide solution by means of permanganate, separates from benzene in crystals, m. p. 261°, reacts with phenylhydrazine or hydroxylamine, and is the lactone of a dioxysantoninic acid.

A syrupy *ketonic acid*, $CO_2H\cdot CO\cdot C_{10}H_{14}(CO_2H)(COMe)\cdot OH$, obtained in the same way as the preceding compound, yields a crystalline *phenylhydrazone*, $C_{15}H_{20}O_5(N_2HPh)_2$, m. p. about 100°, which behaves as a dibasic acid. When treated with lead dioxide, this ketonic acid loses carbon dioxide and yields another *ketonic acid*, which forms a *phenylhydrazone*, $C_{14}H_{20}O_5(N_2HPh)_2$, m. p. 114—116° (decomp.). Under the action of alkaline permanganate solution, the syrupy ketonic acid, $C_{15}H_{20}O_7$, gives oxalic, formic, and acetic acids, together with an unstable acid, which readily loses two carbon atoms and forms a saturated aliphatic acid, *heptanetetracarboxylic acid*,

$$C_6H_{12}(CO_2H)_2{:}C(CO_2H)_2,$$

m. p. 165° (decomp.). When the latter is heated, it loses water and carbon dioxide, yielding the *anhydride*, $C_7H_{13}(C_2O_3)\cdot CO_2H$, m. p. 145°, of a heptanetricarboxylic acid. With water, this anhydride gives an *acid*, $C_{10}H_{16}O_6$, softening at about 88°, and then melting; with sodium hydroxide, the anhydride yields a *heptanetricarboxylic acid*, $C_{10}H_{16}O_6$, m. p. 127°. When the anhydride $C_{10}H_{14}O_5$ is oxidised with chromic and sulphuric acids, it yields succinic acid and a *pentanetricarboxylic acid*, $C_5H_9(CO_2H)_3$, m. p. about 110°, which may be identical with the acid prepared by Emery (Abstr., 1891, 547) and by Perkin (Trans., 1896, 69, 1510).

On heating a crude sample of the heptanetetracarboxylic acid, an *anhydride*, $C_{10}H_{14}O_5$, m. p. 141°, was obtained, which, when boiled with water, yields an *acid*, $C_{10}H_{16}O_6$, m. p. 141°. T. H. P.

The Synthesis of Polypeptides. EMIL FISCHER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 542—553).—The methods employed in the synthesis of polypeptides from amino-acids are not directly applicable when it is required to combine aminohydroxy-acids, owing to the action of phosphorus pentachloride on the hydroxyl group. It is found that the introduction of the carbomethoxyl group gives the necessary protection, the group being afterwards readily removed by hydrolysis. The products are, however, optically inactive.

The reduction of polypeptides with sodium amalgam (this vol., i, 323) gives poor yields, but derivatives of acetals are readily prepared by condensing aminoacetal with chloroacyl chlorides and treated the products with ammonia.

Chloroacetyl-l-*tyrosine methyl carbonate*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot O\cdot CO_2Me,$$

from chloroacetyl-*l*-tyrosine and methyl chlorocarbonate, separates from hot water as an oil, which slowly crystallises in thin, colourless, microscopic leaflets, m. p. 116° (corr.), $[\alpha]_D^{20}$ $+48{\cdot}7°$. It is readily hydrolysed by alkali.

With acetyl chloride and phosphorus pentachloride, it yields *chloroacetyltyrosyl chloride methyl carbonate*, which may be crystallised, but is best condensed, without previous isolation, with glycine ester, yielding *chloroacetyltyrosylglycine ester methyl carbonate*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH(CH_2\cdot C_6H_4\cdot O\cdot CO_2Me)\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

m. p. 130° (corr.), to a clear liquid, after sintering at 125°. The solutions in alcohol or chloroform are optically inactive. Sodium hydroxide hydrolyses it to *chloroacetyltyrosylglycine*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH(CH_2\cdot C_6H_4\cdot OH)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

which crystallises from hot water in small, quadrangular plates, m. p. 188—190° (corr.) (decomp.).

Glycyltyrosylglycine, obtained by the action of ammonia on the above, separates from alcohol in microscopic crystals, m. p. 221° (corr.) (decomp.).

Glycylaminoacetal, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH(OEt)_2$, prepared from aminoacetal and chloroacetyl chloride and heating the chloro-compound thus obtained with aqueous ammonia at 100° or dissolving it in liquid ammonia, separates from light petroleum in deliquescent, colourless crystals, m. p. 45°. The base is strongly alkaline, and does not reduce Fehling's solution. The *hydrochloride* forms microscopic leaflets, m. p. 119° (corr.) (decomp.). The *hydrogen oxalate*, prepared by precipitation in alcoholic solution, has m. p. about 150° (decomp.); the *picrate* crystallises from ethyl acetate in yellow needles. Cold hydrochloric acid converts glycylaminoacetal into glycylglycinaldehyde.

A form of capillary polarimeter tube is described, having a capacity of only 0·1 c.c., and a pyknometer of about the same capacity. It has been found possible to make satisfactory determinations of the rotatory power and density with 0·01—0·02 gram of the substance.

C. H. D.

Condensation Reactions of $\alpha\beta$-Unsaturated Aldehydes. II.

HANS MEERWIN (*Annalen*, 1908, 360, 323—347. Compare this vol., i, 89).—Vorländer (Abstr., 1898, i, 27; 1905, i, 792) found that cinnamaldehyde and crotonaldehyde react readily with methyl sodiomalonate, whilst, on the other hand, Bechert (Abstr., 1894, i, 488) and Hinrichsen (Abstr., 1905, i, 132) prepared cyanocinnamylideneacetic esters and cinnamylidenemalononitrile by condensation of cinnamaldehyde with cyanoacetic esters and malononitrile respectively in presence of sodium ethoxide; hence it was to be expected that $\alpha\beta$-unsaturated aldehydes would condense with methyl malonate in presence of sodium ethoxide to form products of the type $CHR{:}CH{\cdot}CH{:}C(CO_2Me)_2$. It is now found, however, that, in the presence of sodium ethoxide, methyl malonate reacts with 3 mols. of $\alpha\beta$-unsaturated aldehyde, the product having the constitution

$$CH(CO_2Me)_2{\cdot}CHR{\cdot}CH_2{\cdot}CH[CH(CO_2Me)_2]{\cdot}CH(CO_2Me){\cdot}CO_2H.$$

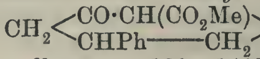
The mechanism of this reaction is discussed, and the conclusion is drawn that the first product is $CH(CO_2Me)_2{\cdot}CHR{\cdot}CH{:}CH{\cdot}CH(CO_2Me)_2$, which, in presence of the alkali, may undergo transformation into $CH(CO_2Me)_2{\cdot}CHR{\cdot}CH_2{\cdot}CH{:}C(CO_2Me)_2$. The present paper contains an account chiefly of the derivatives of cinnamaldehyde.

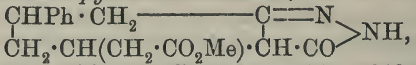
Pentamethyl hydrogen α-phenylpropane-αγγ-trimalonate, $C_{23}H_{28}O_{12}$, prepared from cinnamaldehyde and methyl malonate, crystallises in flat needles, m. p. 119—120°, loses 1 mol. of carbon dioxide at 140—150°, and slowly decolorises permanganate, but not bromine. The *polycarboxylic acid*, obtained on hydrolysis of the ester with dilute sodium hydroxide, is an oil. *Methyl α-phenylpropane-αγγ-trimalonate*, $C_{24}H_{30}O_{12}$, prepared from methyl cinnamylidenemalonate and methyl malonate, or by esterification of the pentamethyl hydrogen ester by means of methyl alcohol and hydrogen chloride, crystallises in monoclinic prisms, m. p. 86—87°.

Knoevenagel and Herz's supposed methyl cinnamylidenedimalonate (Abstr., 1905, i, 63), prepared by the action of cinnamaldehyde on methyl malonate in piperidine solution, is now found to be methyl cinnamylidenemalonate, m. p. 67° (Thiele and Meisenheimer, Abstr., 1899, i, 603).

β-Phenylpimelic-δ acetic acid,

$$CO_2H{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}CH(CH_2{\cdot}CO_2H)_2,$$

is formed together with smaller amounts of 1-*phenyl*cyclo*hexane-3-one-5-acetic acid* when the pentamethyl hydrogen ester is boiled with bromine in aqueous solution until the evolution of carbon dioxide and methyl bromide has ceased. It separates from water in crystalline crusts, m. p. 141—142°, and is not attacked by permanganate or bromine. The *methyl* ester, $C_{18}H_{24}O_6$, is a colourless oil. When boiled with sodium and small amounts of alcohol in toluene solution, this ester is converted into *methyl* 1-*phenyl*cyclo*hexane*-3-*one*-4-*carboxylate*-5-*acetate*,  $CH_2<\begin{matrix}CO\cdot CH(CO_2Me)\\ CHPh\text{——}CH_2\end{matrix}>CH\cdot CH_2\cdot CO_2Me$, which crystallises in white needles, m. p. 139—140°, and does not give a coloration with alcoholic ferric chloride. When heated above its m. p., or on prolonged boiling in alcoholic solution, the keto-ester is transformed into the *enolic* modification, which is crystalline, gives a bluish-violet coloration with ferric chloride, and is unstable, decomposing partly and changing into the keto-ester when brought into contact with water. The *phenylhydrazone* of the keto-ester, $C_{23}H_{26}O_4N_2$, crystallises in yellow needles, m. p. 142—144° (decomp.). When heated with hydrazine hydrate and methyl alcohol, the keto-ester is converted into *methyl* 1-*phenyl*cyclo*hexane*-3 : 4-*pyrazolone*-5-*acetate*,



$$\begin{matrix}CHPh\cdot CH_2\text{————}C{=\!=}N\\ CH_2\cdot CH(CH_2\cdot CO_2Me)\cdot CH\cdot CO\end{matrix}>NH,$$

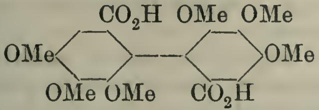
which crystallises in white needles, m. p. 230—231° (decomp.), gives an intense brownish-red coloration with alcoholic ferric chloride, and is soluble in dilute alkalis.

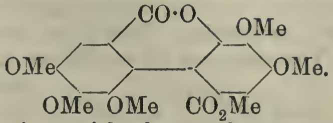
1-Phenyl*cyclo*hexan-3-one-5-acetic acid, $C_{14}H_{16}O_3$, formed by hydrolysis of methyl 1-phenyl*cyclo*hexan-3-one-4-carboxylate-5-acetate with acids, crystallises in white needles, m. p. 118—119°, and is identical with the by-product of the hydrolysis of pentamethyl hydrogen diphenylpropane-αγγ-trimalonate. The *sodium*, *silver*, and *copper* salts are described. The *phenylhydrazone* crystallises in yellow needles, m. p. 166—167° (decomp.). The *methyl* ester, $C_{15}H_{18}O_3$, transparent needles, m. p. 81°. The action of bromine on the acid leads to the formation of hydrogen bromide and a white, crystalline *substance*, m. p. 174° (decomp.), which contains bromine.

Methyl benzylidenedimalonate, $CHPh[CH(CO_2Me)_2]_2$, prepared by condensation of benzaldehyde with methyl malonate in presence of sodium ethoxide (compare Hinrichsen, *loc. cit.*; Staudinger, Abstr., 1905, i, 736), forms prismatic crystals, m. p. 64—65°, and, when hydrolysed with concentrated hydrobromic acid, yields β-phenylglutaric acid, m. p. 142—143° (138°: Vorländer, Abstr., 1902, i, 309; 139·5°: Staudinger, *loc. cit.*).

Methyl o-*nitrobenzylidenedimalonate*, prepared from *o*-nitrobenzaldehyde and methyl malonate, forms white crystals, m. p. 94—95°, and, on hydrolysis with concentrated hydrobromic acid, yields β-*o*-nitrophenylglutaric acid (Abstr., 1907, i, 534). G. Y.

Constitution of Ellagic Acid. JOSEF HERZIG and JULIUS POLAK (*Monatsh.*, 1908, 29, 263—280).—The correctness of Graebe's formula for ellagic acid (Abstr., 1903, i, 262) is further emphasised by the preparation of the following compounds from ellagic acid: 2 : 3 : 4 : 4′ : 5′ : 6′-hexamethoxydiphenyl-6 : 2′-dicarboxylic acid (I), its methyl ester, and the lactone of methyl 2-hydroxy-3 : 4 : 4′ : 5′ : 6′-pentamethoxydiphenyl-6 : 2′-dicarboxylate (II):

I. 

II. 

In carrying out methoxyl determinations with these substances, it was found necessary to add repeatedly small portions of strong hydriodic acid, and to boil until methyl iodide ceased to be evolved; this often required seven to fourteen hours.

Tetramethylellagic acid is readily prepared by acting on ellagic acid with an ethereal solution of diazomethane (compare Goldschmiedt, Abstr., 1905, i, 900). It is converted into a mixture of methyl 2 : 3 : 4 : 4′ : 5′ : 6′-hexamethoxydiphenyl-6 : 2′-dicarboxylate and of the lactone of methyl 2-hydroxy-3 : 4 : 4′ : 5′ : 6′-pentamethoxydiphenyl-6 : 2′-dicarboxylate when boiled for sixteen hours with methyl iodide and potassium hydroxide in alcoholic solution.

Methyl 2 : 3 : 4 : 4′ : 5′ : 6′-*hexamethoxydiphenyl*-6 : 2′-*dicarboxylate*, $C_{12}H_2(OMe)_6(CO_2Me)_2$, crystallises in two forms: small, coarse crystals, m. p. 109—111°, and slender, white needles, m. p. 90—95°. It is hydrolysed when boiled with an alcoholic solution of potassium hydroxide, yielding the *ether acid*, $C_{12}H_2(OMe)_6(CO_2H)_2$, m. p. 240°. Both the ether acid and its methyl ester are converted by hydriodic acid into ellagic acid.

The *lactone* of *methyl* 2-*hydroxy*-3 : 4 : 4′ : 5′ : 6′-*pentamethoxydiphenyl*-6 : 2′-*dicarboxylate*, $C_{13}H_2O_2(OMe)_5{\cdot}CO_2Me$, m. p. 109—111°, when hydrolysed with alcoholic potassium hydroxide, is converted into 2-*hydroxy*-3 : 4 : 4′ : 5′ : 6′-*pentamethoxydiphenyl*-6 : 2′-*dicarboxylic acid*, $OH{\cdot}C_{12}H_2(OMe)_5(CO_2H)_2$, m. p. 200—203° (decomp.). The latter compound, when treated with diazomethane, yields the above mentioned methyl hexamethoxydiphenyldicarboxylate.

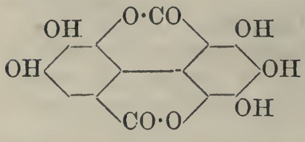
Preparation of Ellagic Acid [with MARIANNE VON BRONNECK.]—The accuracy of Ernst and Zwenger's statement (*Annalen*, 1869, **159**, 32) that ellagic acid is formed on treating ethyl gallate with sodium carbonate or ammonia in the presence of air seemed doubtful, since gallic acid when treated with potassium hydroxide yields galloflavin; their work was therefore repeated, and found to be correct. Ellagic acid is also formed from methyl gallate in the same way. Details are given for obtaining the best yield of ellagic acid from ethyl gallate.

W. H. G.

Resoflavin and its Analogue from Gallic Acid. JOSEF HERZIG and RUDOLF TSCHERNE (*Monatsh.*, 1908, **29**, 281—294. Compare Perkin and Nierenstein, Trans., 1904, **87**, 1412).—A continuation of work previously published (Abstr., 1907, i, 421). When the ether ester, $C_{14}H_3O_2(OMe)_7$, obtained from resoflavin is heated with a dilute potassium hydroxide solution, it is converted into the ether acid, $CO_2H{\cdot}C_{12}H_3(OMe)_5{\cdot}CO_2Me$ (*loc. cit.*), but when heated with strong aqueous potassium hydroxide it yields the ether acid, $C_{12}H_3(OMe)_5(CO_2H)_2$.

Since resoflavin when heated with zinc dust yields fluorene, it is evidently a derivative of diphenyldimetholide; two of the hydroxyl groups probably occupy positions 4 and 4′ in the diphenyl nucleus, but the position of the third is still uncertain.

The analogue of resoflavin obtained from gallic acid by oxidation with ammonium persulphate is shown to be a monohydroxyellagic acid having the annexed constitution, since it is converted into the ether ester, $C_{14}HO_2(OMe)_9$, when treated with potassium hydroxide and methyl iodide; the ether ester on hydrolysis yields the ether acid, $C_{12}H(OMe)_7(CO_2H)_2$.



[With S. Epstein.]—The ether ester, $C_{14}H_3O_2(OMe)_7$ (Herzig and Tscherne, *loc. cit.*), when boiled with a strong solution of potassium hydroxide in dilute alcohol, is converted into 3 (or 5) : 2 : 4 : 4′ : 6′-*pentamethoxydiphenyl*-6 : 2′-*dicarboxylic acid*, $C_{12}H_3(OMe)_5(CO_2H)_2$, crystallising in white needles, m. p. 247—249°.

[With Marianne von Bronneck.]—The product obtained by the oxidation of gallic acid with persulphate (flavellagic acid) is converted by diazomethane into the *ether ester*, $C_{14}HO_4(OMe)_5$, m. p. 245°. It is converted by methyl iodide and potassium hydroxide into *methyl* 3 : 4 : 5 : 6 : 2′ : 3′ : 4′-*heptamethoxydiphenyl*-2 : 6′-*dicarboxylate*,

$$C_{12}H(OMe)_7(CO_2Me)_2,$$

m. p. 83—87°, which, on hydrolysis with potassium hydroxide, yields the *acid*, $C_{12}H(OMe)_7(CO_2H)_2$, m. p. 163—167°; it crystallises with $1H_2O$, and then has m. p. 95—100° (decomp.). W. H. G.

Glaucohydroellagic Acid. Maximilian Nierenstein (*Ber.*, 1908, **41**, 1649—1650).—With the object of ascertaining whether ellagic acid on reduction behaves like tannin (compare Nierenstein, this vol., i, 90), the formation of glaucohydroellagic acid from ellagic acid has been investigated (compare Rembold, this Journ., 1876, i, 592). It is found that glaucohydroellagic acid is identical with pentahydroxydiphenylmethylolide, described by A. G. Perkin and Nierenstein (Trans., 1905, **87**, 1420). W. H. G.

Xanthophanic Acid. IV. [Carl Liebermann and Simon Lindenbaum (*Ber.*, 1908, **41**, 1607—1619. Compare Abstr., 1906, i, 556; 1907, i, 889).—It was shown previously that the bromophenylhydrazone prepared from the "transformation product" of xanthophanic acid is a derivative, not of this, but of methyl resacetophenonecarboxylate. This is now found to be the case also with the hydrazone formed by the action of hydrazine on the "transformation product." When heated alone or with glacial acetic acid, the hydrazone,

$$CO_2Me{\cdot}C_6H_2(OH)_2{\cdot}CMe{:}N{\cdot}NH_2,$$

yields hydrazine and a lemon-yellow compound, which must have the constitution $N_2[CMe{\cdot}C_6H_2(OH)_2{\cdot}CO_2Me]_2$, as when boiled with dilute sulphuric acid it forms hydrazine, methyl alcohol, and resacetophenone. These substances have now been prepared synthetically.

Resorcinol dimethyl ether is converted by means of hydrogen cyanide and hydrochloric acid into β-resorcylaldehyde dimethyl ether, which is oxidised by potassium permanganate, forming β-resorcylic acid dimethyl ether, $CO_2H\cdot C_6H_3(OMe)_2$ [$CO_2H : OMe : OMe = 1 : 2 : 4$]. An acetyl group is introduced into this by means of acetyl chloride and aluminium chloride, and finally the methyl groups are removed by treatment with hydriodic acid. This series of changes has been carried out also, starting from resorcinol diethyl ether. The resulting acid is identical with resacetophenonecarboxylic acid, which is obtained from the "transformation product" of xanthophanic acid methyl or ethyl ether, and must have the constitution

$$[CO_2H : OH : OH : COMe = 1 : 2 : 4 : 5].$$

The methyl ester of the synthetical acid yields a *p*-bromophenylhydrazone identical with that obtained from the "transformation product." On the other hand, the hydrazone obtained from the synthetical methyl ester differs from that prepared from the "transformation product" both in its m. p. and in its solubility. It is considered that these hydrazones may be stereoisomerides, the more that the lemon-yellow products obtained on heating the hydrazones are identical.

When heated with ethyl ethoxymethyleneacetoacetate and small amounts of sodium ethoxide in alcoholic solution, ethyl resacetophenonecarboxylate yields traces of xanthophanic and glaucophanic acids, but the chief product is an *acid*, $C_{16}H_{14}O_7$, which crystallises in needles, m. p. 164—165°.

The p-*bromophenylhydrazone* of ethylxanthophanic acid,

$$C_{18}H_{20}O_7\colon N\cdot NH\cdot C_6H_4Br,$$

prepared from ethylxanthophanic acid and *p*-bromophenylhydrazine in benzene solution, crystallises in red needles, m. p. 180—181°, decomposes on prolonged boiling with alcohol, and gives a yellowish-green fluorescence with concentrated sulphuric acid.

The products of each stage of the synthesis of resacetophenonecarboxylic acid were isolated and are described. The following are new.

Resacetophenonecarboxylic acid dimethyl ether,

$$COMe\cdot C_6H_2(OMe)_2\cdot CO_2H,$$

crystallises in prisms, m. p. 231—233°. The *diethyl ether*, m. p. 190—202°, was obtained mixed with the *monoethyl ether*.

Methyl resacetophenonecarboxylate crystallises in needles, m. p. 124°. The *ethyl* ester, colourless needles, m. p. 94°. The *p*-bromophenylhydrazone of the methyl ester, m. p. 227—228° (224°: *loc. cit.*).

The *hydrazone*, prepared by the action of hydrazine on the "transformation product" of ethylxanthophanic acid, crystallises in white needles, m. p. 138°, decomp. 150—160°, forming the lemon-yellow *azine*, $C_{20}H_{20}O_8N_2$, m. p. 327°. The *hydrazone*, obtained from the synthetical methyl ester, forms yellowish-green crystals, m. p. 170°, changing into the lemon-yellow azine, m. p. 327°. G. Y.

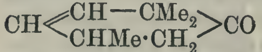
Condensation of *o*-Nitrobenzaldehyde with Aromatic Hydrocarbons in Presence of Concentrated Sulphuric Acid. ALFRED KLIEGL (*Ber.*, 1908, 41, 1845—1851. Compare this vol., i, 82).—*m*- and *p*-Nitrobenzaldehyde condense with benzene in presence of concentrated sulphuric acid to form *m*- and *p*-nitrotriphenylmethane (Baeyer and

Tchacher, Abstr., 1887, 44; 1888, 373; 1890, 1141), but the author finds that the reaction proceeds quite differently when *o*-nitrobenzaldehyde is used, *o*-nitrophenyl *p*-tolyl ketone and *p*-tolylanthroxan being obtained from toluene, and phenylanthroxan with but a trace of *o*-nitrobenzophenone (in one experiment) from benzene. To confirm these results, o-*nitrophenyl* p-*tolyl ketone* was synthesised by oxidising o-*nitrophenyl*-p-*tolylmethane* (yellow oil, b. p. 195—198°/12 mm., prepared from *o*-nitrobenzyl chloride and toluene in presence of aluminium chloride) with sodium dichromate and glacial acetic acid. It forms thin, colourless prisms, m. p. 155°. On oxidation, it yields 2′-*nitro*-4-*benzoylbenzoic acid*, shining plates, m. p. 235·5—236°, and on reduction with tin and glacial acetic acid, p-*tolylanthroxan*, $C_{14}H_{11}ON$, yellow crystals, m. p. 95·5°. J. C. C.

The Reaction between Potassium Cyanide and *o*-Nitrobenzaldehyde. JOAN POPOVICI (*Ber.*, 1908, 41, 1851—1853).—By the interaction of potassium cyanide and *o*-nitrobenzaldehyde, the author obtained (Abstr., 1907, i, 628) 2 : 2′-dinitrobenzoin, but Ekecrantz and Ahlquist (this vol., i, 347) stated that the product of the reaction was a mixture of *o*-nitrosobenzoic acid and *o*-azoxybenzoic acid. The author has now repeated the experiment under the same conditions, and confirms the former result. 2 : 2′-Dinitrobenzoin has m. p. 161—162° (corr.), and not 155·5° (corr.) as previously given. J. C. C.

Synthesis of Pulenone Derivatives from *o*-Cresol. KARL AUWERS and MAX HESSENLAND (*Ber.*, 1908, 41, 1790—1816).—The product, $C_9H_{12}OCl_2$ (Abstr., 1906, i, 947), obtained by the action of magnesium methyl iodide on 2-keto-1-methyl-1-dichloromethyl-$\Delta^{2,5}$-*cyclo*hexadiene, is shown to be a ketone, although it gives none of the characteristic reactions of ketones, probably owing to the inhibiting effect of the $-CHCl_2$ group. When reduced for several days with acetic acid and zinc dust, it yields the *ketone*, $C_9H_{14}O$, in the form of a liquid, b. p. 63—65°/16 mm. or 172—174°/757 mm., with an odour of peppermint.

The corresponding *semicarbazone*, $C_{10}H_{17}ON_3$, crystallises from a mixture of benzene and light petroleum in glistening needles, m. p. 129°. The ketonic nature of these products indicates that the magnesium methyl iodide has added itself to the double bond, and not to the carbonyl group, so that the original condensation product is 1 : 4-*dimethyl*-4-*dichloromethyl*-Δ^5-cyclo*hexen*-3-*one*, and the reduction product, 1 : 4 : 4-*trimethyl*-Δ^5-cyclo*hexen*-3-*one* or *βγ-pulenenone*,

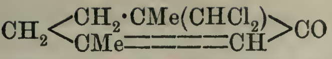


$$\mathrm{CH}{<}\genfrac{}{}{0pt}{}{\mathrm{CH-CMe_2}}{\mathrm{CHMe\cdot CH_2}}{>}\mathrm{CO}$$

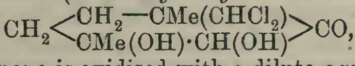
(compare Wallach, 1904, i, 74).

The optical properties of the compounds are in complete harmony with these formulæ. When reduced with sodium and alcohol, βγ-pulenenone yields an unsaturated alcohol, *βγ-pulenenol*, $C_9H_{16}O$, as a clear, mobile liquid, b. p. 82—85°/15 mm. or 189°/754 mm. It has $D_4^{18\cdot5}$ 0·9209 and $n_D^{18\cdot5}$ 1·47398, and when oxidised with chromic anhydride yields βγ-pulenenone.

The product obtained by the action of concentrated sulphuric acid on dichloro-βγ-pulenenone is the isomeric *dichloro-αβ-pulenenone*,

 $CH_2<\begin{matrix}CH_2\cdot CMe(CHCl_2)\\ CMe{=\!=\!=\!=\!=}CH\end{matrix}>CO$ (compare Abstr., 1906, i, 947), and when reduced with acetic acid and zinc dust yields *αβ-pulenenone* as an oil, b. p. 86—88°/15 mm. or 208°/753 mm. It has D_4^{16} 0·9317 and $n_D^{16.5}$ 1·47958. Its *semicarbazone* crystallises from methyl alcohol in flat, glistening prisms, m. p. 200—201°. When reduced, the αβ-ketone yields a saturated alcohol, pulenol, probably identical with Wallach's pulenol, as when oxidised it yields pulenone. The formation of this saturated alcohol is in harmony with the view that αβ-pulenenone has the ethylene linking in the αβ-position with respect to the carbonyl group. An examination of the oxidation products also supports this view. When oxidised with permanganate at 0—10°, αβ-pulenenone yields a mixture of Wallach's αα-dimethyl-γ-acetylbutyric acid, the semicarbazone of which has m. p. 169° (Wallach: 163°), and *ααδ-trimethyl-δ-hydroxyadipic acid,* m. p. 145—148°, which is insoluble in benzene. A bimolecular reduction *product*, $C_{18}H_{26}O_2Cl_4$, is obtained when dichloro-αβ-pulenenone is reduced with sodium amalgam, alcohol, and dilute acetic acid; a small amount is also formed during the reduction with zinc dust and acetic acid. It crystallises from alcohol, and has m. p. 215—225°.

Dichloro-αβ-pulenenone reacts with magnesium methyl iodide, yielding 1:1:4-*trimethyl*-4-*dichloromethyl*cyclo*hexan*-3-*one*, $C_{10}H_{16}OCl_2$, which has b. p. 135—145°/17—18 mm., m. p. 73°.

Dihydroxydichloropulenone (1:2-*dihydroxy*-1:4-*dimethyl*-4-*dichloromethyl*cyclo*hexan*-3-*one*),  $CH_2<\begin{matrix}CH_2{-}CMe(CHCl_2)\\ CMe(OH)\cdot CH(OH)\end{matrix}>CO$, is formed when dichloro-αβ-pulenenone is oxidised with a dilute aqueous acetone solution of permanganate in the presence of acid. It crystallises from water in compact prisms containing $1H_2O$; it melts at 70°, then solidifies, and melts again at 113°. Its *monobenzoyl* derivative, $C_{16}H_{18}O_4Cl_2$, has m. p. 182—183°. J. J. S.

Conversion of Dichloro-αβ-pulenenone into $\Delta^{1:3}$-Dihydro-*p*-xylene. Karl Auwers and Max Hessenland (*Ber.*, 1908, 41, 1816—1827).—When dichloro-αβ-pulenenone (preceding abstract) is warmed with alcoholic potash, the chief products are a monobasic unsaturated acid, $C_9H_{13}O_2Cl$, an unsaturated acid, $C_9H_{12}O_2$, and a hydrocarbon, C_8H_{12}. The chlorinated acid is formed in small quantities only, probably according to the equation $C_9H_{12}OCl_2 + H_2O \longrightarrow C_9H_{13}O_2Cl + HCl$; it crystallises from light petroleum, has m. p. 141·5°, and is probably 3-*chloro*-1:4-*dimethyl*-Δ^1-cyclo*hexene*-2-*carboxylic acid.* The acid $C_9H_{12}O_2$ can be obtained in larger quantity, and is 1:4-*dimethyl*-$\Delta^{1,3}$-cyclo*hexadiene*-2-*carboxylic acid.* It is best purified by conversion into the methyl ester and subsequent hydrolysis with alcoholic potassium hydroxide. The acid crystallises from dilute methyl alcohol or from light petroleum in glistening, flat plates, m. p. 40—42°. It is volatile with steam, but when heated alone to 155—175°, or when boiled with oxalic acid solution or with alkalis, carbon dioxide is eliminated and the hydrocarbon C_8H_{12} formed. The acid combines with bromine, and the dibromide when heated with alcoholic potassium hydroxide yields 2:5-dimethylbenzoic acid. The *methyl* ester, $C_{10}H_{14}O_2$, has b. p. 79—81°/10 mm., D_4^{20} 0·997, n_D^{18} 1·47643, and it is only slowly polymerised.

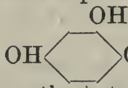
$\Delta^{1,3}$-*Dihydro*-p-*xylene* (1 : 4-*dimethyl*-$\Delta^{1,3}$-cyclo*hexadiene*) is a clear, mobile liquid with an ethereal odour. It has D_4^{20} 0·832, $n_D^{19·6}$ 1·478.

The hydrocarbon yields a dibromide, m. p. 240—247°, and when nitrated yields trinitro-*p*-xylene. The constitution of the hydrocarbon follows from the formation of this nitro-derivative, and from the fact that acetonylacetone and acetone are found among its products of oxidation. The two ketones were isolated in the form of their *p*-nitrophenylhydrazones. *Acetonylacetone* p-*nitrophenylosazone*,

$$C_2H_4(CMe{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2)_2,$$

crystallises from glacial acetic acid or boiling amyl alcohol, and has m. p. 210—212°. J. J. S.

Derivatives of Resacetophenone. WILLY DAHSE (*Ber.*, 1908, 41, 1619—1625).—The compounds described were prepared in order to compare them with the resacetophenone derivatives obtained from xanthophanic acid (compare this vol., i, 548). *Resacetophenonehydrazone*,



$OH \cdot C_6H_3(OH) \cdot CMe{:}N{\cdot}NH_2$, obtained by the action of hydrazine hydrate on the ketone in absolute alcohol, crystallises in white needles; on boiling with glacial acetic acid or heating at 125°, the *azine*,

$$C_{16}H_{16}O_4N_2,$$

is formed, crystallising from nitrobenzene in yellow needles, m. p. 307°. Resacetophenone gives only a monoacetate on boiling with sodium acetate and acetic anhydride (m. p. 72—73°, Nencki and Sieber, Abstr., 1881, 591), the *phenylhydrazone*, $C_{16}H_{16}O_3N_2$, of which forms golden-yellow needles, m. p. 130°. Bromination of resacetophenone gives 3:5-*dibromoresacetophenone*, $C_6HBr_2(OH)_2{\cdot}COMe$, crystallising in needles, m. p. 173—174°; the *hydrazone*, $C_8H_8O_2N_2Br_2$, forms glistening, white needles, and at 145° or on heating with glacial acetic acid passes into the *azine*, $C_{16}H_{12}O_4N_2Br_4$, yellow needles, m. p. 340°; the *phenylhydrazone*, $C_{14}H_{12}O_2N_2Br_2$, crystallises in white needles, m. p. 162°. Benzylidene derivatives are obtained on heating the dibromoresacetophenone with the aldehyde and concentrated sulphuric acid at 100°; *benzylidenedibromoresacetophenone*,

$$C_6HBr_2(OH)_2{\cdot}CO{\cdot}CH{:}CHPh,$$

forms greenish-yellow needles, m. p. 165°; the *m*- and p-*nitrobenzylidene* derivatives, $C_{15}H_9O_5NBr_2$, are greenish-yellow, and have m. p. 236° (decomp.) and 228° respectively.

Dibromoresacetophenone diacetate, $C_{12}H_{10}O_5Br_2$, crystallises from alcohol in needles, m. p. 104—105°, and on oxidation with chromic acid in acetic acid gives 3:5-dibromo-2:4-dihydroxybenzoic acid (Zehenter, Abstr., 1882, 193), a result which establishes the position of the bromine atoms in dibromoresacetophenone.

Bromodinitrodihydroxybenzoic acid, $C_6Br(NO_2)_2(OH)_2{\cdot}CO_2H$, obtained when dibromoresacetophenone is warmed with three times its weight of nitric acid (D 1·4), crystallises from water in yellow needles, m. p. 187°; the *silver* salt, $C_7H_2O_8N_2BrAg$, is an unstable, orange-yellow powder; the *methyl* ester, $C_8H_5O_8N_2Br$, forms white needles, m. p. 100°.

When, however, the dibromoresacetophenone is kept cool during nitration, *bromodinitroresacetophenone*, $C_8H_5O_7N_2Br$, is formed, which crystallises in yellowish-white needles, m. p. 148°; the *potassium* and *sodium* salts are golden-yellow; the *diacetate*, $C_{12}H_9O_9N_2Br$, crystallises in white needles, m. p. 177°; the *phenylhydrazone*,

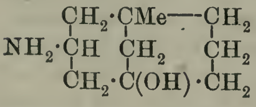
$$C_{16}H_{11}O_6N_4Br,$$

in red needles, m. p. 236°; the *hydrazone*, $C_8H_7O_6N_4Br$, in brown needles, decomp. 161°; the *azine*, $C_{16}H_{10}O_{12}N_6Br_2$, is yellow, m. p. 320°. W. R.

1 : 5-Diketones. III. PAUL RABE (*Annalen*, 1908, **360**, 265—288. Compare Abstr., 1904, i, 747).—The author has continued his work on the synthesis of dicyclic keto-alcohols containing a bridged linking by transformation of semi-cyclic 1 : 5-diketones.

Transformation of Ethyl γ-Benzoyl-α-acetyl-βγ-diphenylbutyrate into a Cyclic Keto-alcohol [With RICHARD EHRENSTEIN.]—When deoxybenzoin is condensed with ethyl benzylideneacetoacetate in presence of sodium ethoxide, the *sodium* compound of *ethyl γ-benzoyl-α-acetyl-βγ-diphenylbutyrate* is obtained, which, on treatment with ice-cold dilute sulphuric acid, yields the *ester* as a pale yellow, viscous oil, giving a violet coloration with alcoholic ferric chloride. This, slowly when alone, or more rapidly by treatment with alcohol, is transformed into ethyl 1 : 2 : 3-triphenyl*cyclo*hexan-1-ol-5-one-4-carboxylate, m. p. 123°, alcoholic solutions of which, when freshly prepared, do not give a reaction with ferric chloride, but when boiled for some time give a violet coloration. The substance therefore, on boiling, is partly converted into an *enolic* modification; this is obtained as a viscous oil by treating the sodium derivative with dilute sulphuric acid. It is quickly converted into the ketonic form in presence of alcohol. *Ethyl* 2 : 3 : 4-*triphenyl*-1 : 6-*dimethyl*-1 : 4-*dihydropyridine*-5-*carboxylate*, obtained by mixing the sodium compound of ethyl γ-benzoyl-α-acetyl-βγ-diphenylbutyrate with methylamine hydrochloride in alcoholic methylamine solution, has m. p. 88°. *Ethyl* 5-*methylimino*-1 : 2 : 3-*triphenyl*cyclo*hexan*-1-*ol*-4-*carboxylate*, m. p. 108°, results on mixing ethyl 1 : 2 : 3-triphenyl*cyclo*hexan-1-ol-5-one-4-carboxylate with alcoholic methylamine.

Dicyclic Alcohols with Bridged Linkings [With MAX JAHR.]—Methyl*dicyclo*nonanolone (Abstr., 1904, i, 509), on treatment with hydroxylamine, furnishes two stereoisomeric oximes. The *α-oxime*, which separates on pouring the mixture on to ice, has m. p. 201°, and contains benzene of crystallisation when crystallised from this solvent. On reduction with sodium and alcohol, it yields the corresponding *α-amine*, m. p. 202—204°. The *β-oxime*, isolated from the mother liquor, has m. p. 145°, and on reduction furnishes the *β-amine*, m. p. 86—87°. Both these amines have the composition of a 7-*amino*-1-*methyl*dicyclo-[1 : 3 : 3]-*nonan*-5-*ol* (annexed formula). The β-amine forms a *hydrochloride*, m. p. 272—275° (decomp.), a yellow *picrate*, decomp. 238°, a *picrolonate*, decomp. 285—286°, and a *methiodide*, decomp. 278°.



$$\begin{array}{lll} & CH_2\cdot CMe & —CH_2 \\ & | & | \\ NH_2\cdot CH & CH_2 & CH_2 \\ | & | & | \\ & CH_2\cdot C(OH) & \cdot CH_2 \end{array}$$

1 : 3-*Dimethyl*dicyclo-[1 : 3 : 3]-*nonan*-5-*ol*-7-*one*, obtained by condensing dimethyl*cyclo*hexenone and ethyl acetoacetate in presence of sodium ethoxide, has m. p. 85°, and b. p. 160—170°/9—10 mm. On reduction with sodium and alcohol, it gives 1 : 3-*dimethyl*dicyclo-[1 : 3 : 3]-*nonan*-5 : 7-*diol*, m. p. 195°, and on treatment with hydriodic acid and phosphorus, 1 : 3-*dimethyl*dicyclo-[1 : 3 : 3]-*nonane*, a colourless, volatile liquid, b. p. 195—200°/750 mm. Dimethyl*dicyclo*nonanolone forms an *α-oxime*, m. p. 186—187°, and a *β-oxime*, m. p. 140—141°. The former gives the corresponding *α-amine*, m. p. 203—204°, and the latter the *β-amine*, m. p. 155°. The *hydrochloride*, decomp. at 265—268°, the *picrate*, m. p. 225—227° (decomp.), the *picrolonate*, decomp. at 274—275°, and the *methiodide*, decomp. at 220—223°, of the latter were prepared. J. C. C.

Method for the Determination of the Configuration of α-Dioximes. Leo Tschugaeff (*Ber.*, 1908, 41, 1678—1684. Compare Abstr., 1905, i, 743).—The fact that, of the various stereoisomerides of an α-dioxime, the *syn*-modification alone yields complex metallic dioximines is utilised for the determination of the configuration of dioximes. Stierlin's α-anisildioxime (Abstr., 1889, 512), Hoffmann's α-cuminildioxime (Abstr., 1890, 1143), and α-furildioxime (m. p. 166—168°) are thus shown to possess the *syn*-configuration, whilst Werner and Bloch's two stereoisomeric *o* : *o*′-dichlorobenzildioximes (Abstr., 1899, i, 753), which do not form coloured complex metallic derivatives, must be the *amphi*- and the *anti*-modifications.

An interesting illustration of the method is given by Boeris' stereoisomeric methylanisylglyoxaldioximes (Abstr., 1894, i, 72). The modification, m. p. 125°, obtained by Angeli's method of reducing the corresponding peroxide, is probably the *amphi*-dioxime, and, in accordance with the rule, does not form dioximines. By heating, it is transformed into an isomeride, m. p. 207°, which does yield dioximines, and has consequently the *syn*-configuration, although Angeli's researches on purely aromatic peroxides show that the *amphi*-dioximes obtained by reduction are converted into *anti*-dioximes by heat. An explanation is offered of the abnormal behaviour of the preceding aliphatic aromatic dioxime. The *nickel* and the *ferrodipyridine* dioximines of α-anisildioxime and of α-furildioxime are described shortly. C. S.

Diethoxybenzoquinone. Jacques Pollak and J. Goldstein (*Monatsh.*, 1908, 29, 135—138).—Will has stated (Abstr., 1888, 457) that some dimethoxybenzoquinone is formed on adding pyrogallol trimethyl ether to concentrated nitric acid, whilst according to Schiffer (Abstr., 1892, 715) pyrogallol triethyl ether is not converted into diethoxybenzoquinone when added to nitric acid in glacial acetic acid.

This difference in the behaviour of the two ethers has been further investigated. Schiffer's work has been repeated and confirmed; when, however, the trimethyl ether is treated in the same way, it is partly converted into dimethoxybenzoquinone. It is also found that if the mixture of nitric and glacial acetic acids is added to a solution of pyrogallol triethyl ether in glacial acetic acid, some diethoxybenzoquinone is formed. The latter compound crystallises in wide needles, m. p. 124—126° (compare Weidel and Pollak, Abstr., 1900, i, 290). W. H. G.

Bornyl Palmitate. O. von Sobbe (*J. pr. Chem.*, 1908, [ii], 77, 510—512).—Bornyl palmitate is best prepared by the action of palmityl chloride, which has been distilled over sodium, on the sodium derivative of borneol in boiling ethereal solution. The borneol should first be freed from *iso*borneol by the alcohol-sulphuric acid method. The ester crystallises in glistening, white scales, m. p. 67—68°. G. Y.

Preparation of Acetals by Claisen's Method. Alexander E. Arbusoff (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 637—652).—Part of this paper has been already published (Abstr., 1907, i, 749).

The action of ethyl orthoformate on menthone or pulegone in presence of sulphuric acid yields the unstable acetal of menthone or pulegone, which, under the conditions of experiment, decomposes, giving ordinary alcohol and the ether corresponding with an unsaturated alcohol. Thus menthone yields the *ether*, $C_{10}H_{17}\cdot OEt$, b. p. 83—84°/9 mm., D_0^{20} 0·8749, and pulegone the *ether*, $C_{10}H_{15}\cdot OEt$, b. p. 97—97·5°/12 mm., D_0^{20} 0·9047.

Camphoracetal, $C_{10}H_{16}(OEt)_2$, prepared by the action of ethyl orthoformate on camphor in presence of sulphuric acid, is an almost colourless liquid, b. p. 119—120°/16·5 mm., D_0^0 0·9632, D_0^{22} 0·9462. Besides camphoracetal, this reaction gives a *compound*, b. p. 82—83°/15 mm., which contains C, 72·73% and H, 10·62%, and is probably a compound of camphor and alcohol analogous with the so-called chloral alcoholate.

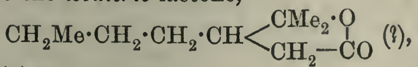
Methylmenthone, $C_{11}H_{22}O$, prepared by the action of magnesium methyl iodide on menthone, is a colourless, pleasant-smelling liquid, b. p. 103°/17 mm., 215·5°/749·6 mm., D_0^0 0·9121, D_0^{19} 0 8970. T. H. P.

Chemical Action of Light. XII. Giacomo L. Ciamician and Paul Silber (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 576—582; *Ber.*, 1908, 41, 1928—1935. Compare Abstr., 1907, i, 587; this vol., i, 277).—When dissolved in aqueous alcohol and subjected to the prolonged action of light, dihydrocarvone, like other *cyclo*ketones (*loc. cit.*), yields an aliphatic acid and an aldehyde, whilst carvone is almost completely converted into an isomeric compound under the same conditions.

The products yielded by dihydrocarvone are (1) the *acid*,

$$CH_2Me\cdot CH_2\cdot CH_2\cdot CH(CMe{:}CH_2)\cdot CH_2\cdot CO_2H\ (?),$$

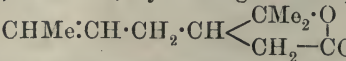
which is an oily liquid, b. p. 135—137°/12 mm., 254·5°/758 mm., and, when boiled with sulphuric acid diluted with its own volume of water, is transformed into the *isomeric* lactone,



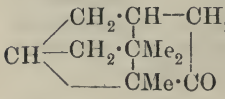
$$CH_2Me\cdot CH_2\cdot CH_2\cdot CH<\begin{array}{ll}CMe_2\cdot & O\\ & |\\ CH_2- & CO\end{array}\ (?),$$

b. p. 264—265°; (2) an aldehyde,

$$CHMe{:}CH\cdot CH_2\cdot CH(CMe{:}CH_2)\cdot CH_2\cdot CHO$$

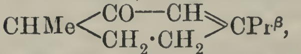
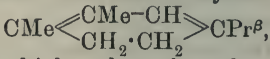
which was not separated, but was converted into the corresponding hydroxamic acid, and this, by boiling with aqueous sulphuric acid, into the *lactone*,  $CHMe{:}CH\cdot CH_2\cdot CH<\begin{matrix}CMe_2\cdot O\\ CH_2-CO\end{matrix}$, b. p. 266—267°.

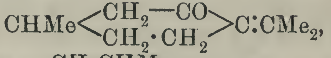
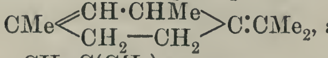
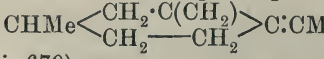
Carvone yields (1) an isomeric *compound* (annexed formula), m. p. 100°, b. p. 206·5°, which has the normal molecular weight in freezing acetic acid and closely resembles camphor in odour and appearance; its *oxime*, $C_{10}H_{14}{:}NOH$, m. p. 126—128°, separates from light petroleum in large, monoclinic crystals [Boeris: $a:b:c = 1{\cdot}1057:1:0{\cdot}6233$; $\beta = 67°36'$], and its *semicarbazone*, $C_{11}H_{17}ON_3$, crystallises from alcohol in large prisms, m. p. 239°; (2) a small proportion of an oily *compound*, $C_{10}H_{16}O$ or $C_{10}H_{18}O$; b. p. 218—223°, which has an odour resembling that of roses.


(?)

T. H. P.

Action of Magnesium Methyl Iodide on Carvenone and Pulegone.

Hans Rupe and F. Emmerich (*Ber.*, 1908, 41, 1750—1754).—The action of magnesium methyl iodide on carvenone,  $CHMe<\begin{matrix}CO-CH\\ CH_2\cdot CH_2\end{matrix}>CPr^{\beta}$, leads to the formation of an unstable, tertiary alcohol, which loses water, forming an unsaturated hydrocarbon, which must be 2-methylcarvenene,  $CMe<\begin{matrix}CMe-CH\\ CH_2\cdot CH_2\end{matrix}>CPr^{\beta}$, since its molecular refraction is considerably higher than the calculated, as is also that of carvenone. It has been shown by other authors (Wallach, Abstr., 1895, i, 672; 1904, i, 752; 1905, i, 450; Knoevenagel, Abstr., 1897, i, 606) that in regard to their molecular refractions, $\alpha\beta$-unsaturated ketones resemble alcohols with two ethylene linkings. The high molecular refraction of the unsaturated hydrocarbon agrees with the presence of two conjugated ethylene linkings. The hydrocarbons obtained in the same manner from carvone, dihydrocarvone, pulegone, and *iso*pulegone (this vol., i, 433), which contain an ethylene linking in the 4(8)- or (8)(9)-position, have normal refractions, and hence cannot contain conjugated ethylene linkings.

The hydrocarbon obtained by the action of methyl iodide on pulegone,  $CHMe<\begin{matrix}CH_2-CO\\ CH_2\cdot CH_2\end{matrix}>C{:}CMe_2$, must be 3-methyl-$\Delta^{4(8)}$-menthadiene,  $CMe<\begin{matrix}CH\cdot CHMe\\ CH_2-CH_2\end{matrix}>C{:}CMe_2$, and not 3-methylene-$\Delta^{4(8)}$-terpene,  $CHMe<\begin{matrix}CH_2\cdot C(CH_2)\\ CH_2-CH_2\end{matrix}>C{:}CMe_2$, as stated by Grignard (Abstr., 1901, i, 679).

2-*Methylcarvenene*, $C_{11}H_{18}$, is a colourless, mobile oil, b. p. 86—87°/10 mm., D^{20} 0·8563, n_D^{20} 1·49613, $[\alpha]_D$ +0·67°, has a sweet flavour, and is not reduced by sodium and boiling amyl alcohol. As the hydrocarbon does not contain an asymmetric carbon atom, the small rotatory power must result from the presence of an impurity.

3-*Methyl*-$\Delta^{4(8)}$-*menthadiene*, $C_{11}H_{18}$, is a colourless, mobile oil, b. p.

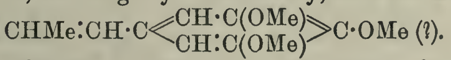
71—73°/10 mm., D^{20} 0·8402, n_D^{20} 1·47252, $[\alpha]_D^{20}$ $-81·41°$, $-96·89°$, is not reduced by sodium and amyl alcohol, and when oxidised by potassium permanganate yields acetone and an *acid*, which crystallises in white prisms, m. p. 153—154°. A mixture of this acid with adipic acid, m. p. 149—150°, had m. p. 120—127°. G. Y.

Isomerisation Phenomena during the Preparation of Cadinene. Nicolaus Lepeschkin (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 698—699).—In order to investigate the genetic relations of the sesquiterpenes obtained from oleum cadinum, the author has studied the actions of hydrogen chloride and acetic acid on cadinene.

Cadinene dihydrochloride decomposes on heating, yielding cadinene exhibiting the following constants: b. p. 148—149°/20 mm., D_4^{20} 0·9172, n_D 1·5107, $[\alpha]_D$ $-111·28°$. But on prolonged heating in a sealed tube at 180—200°, cadinene dihydrochloride undergoes isomeric change into an unstable chloride, which yields a sesquiterpene having b. p. 145—148°/20 mm., D_4^{20} 0·9061, n_D^{20} 1·5041, and $[\alpha]_D$ $-2·80°$; this sesquiterpene is probably identical with the one obtained by Schindelmeiser (this vol., i, 353), and is isomeric with the one previously obtained by the author (this vol., i, 278) by the action of hydriodic acid on the sesquiterpene having $[\alpha]_D$ $-14·12°$.

When cadinene is heated with acetic acid at 180—200°, its rotation falls from $-111·28°$ to $-8°$; the products formed have not been investigated.

The purest cadinene prepared by the author was obtained by the action of sodium ethoxide on the dihydrochloride, and has the following constants: b. p. 149°/20 mm. and 271—272° at ordinary pressure, D_4^{20} 0·9183, n_D^{20} 1·5073, and $[\alpha]_D$ $-110·96°$. T. H. P.

Constituents of Essential Oils. Elemicin, a High-boiling Constituent of Elemi Oil, and the Displacement of Alkyloxy-groups in the Benzene Nucleus by Hydrogen. Friedrich W. Semmler (*Ber.*, 1908, **41**, 1768—1775).—The author has investigated the composition of the fraction of crude elemi oil which has the highest boiling point. The specimen studied had D^{20} 1·031, n_D 1·5188, and on analysis gave figures pointing to the presence of a benzene derivative, accompanied by small amounts of a sesquiterpene alcohol. A fraction, b. p. 150—156°/10 mm., obtained on further distillation over sodium, had D^{20} 1·036, n_D 1·54193, was slightly lævorotatory, and is considered to consist of *elemicin*,  $CHMe{:}CH{\cdot}C\left<\begin{matrix}CH{\cdot}C(OMe)\\ CH{:}C(OMe)\end{matrix}\right>C{\cdot}OMe$ (?). The propenyl group may be formed by intramolecular change of an allyl group during the distillation over sodium. When reduced with sodium and alcohol, elemicin yields an optically inactive *product*, $C_{12}H_{18}O_2$ (?), b. p. 125·5°/10 mm., D^{20} 0·994, n_D 1·151200. Oxidation of elemicin by means of potassium permanganate in acetone solution leads to the formation of 3 : 4 : 5-trimethoxybenzoic acid. When treated with sodium and alcohol, this acid is reduced to *m*-methoxybenzoic acid. *o*-Methoxybenzoic, veratric, asaronic, and myristic acids, on the other hand, are not reduced by sodium and alcohol. G. Y.

Constituents of Essential Oils. Elemicin and *iso*Elemicin. Friedrich W. Semmler (*Ber.*, 1908, **41**, 1918—1921. Compare preceding abstract).—When treated with ozone in moist benzene solution, elemicin, which has not been distilled over sodium, yields trimethylhomogallaldehyde and trimethylhomogallic acid, but after distillation over sodium it yields trimothylgallaldehyde. Elemicin therefore contains an ethylene linking in the $\beta\gamma$-position in the side-chain, and, when distilled over sodium, undergoes isomerisation into *iso*elemicin, which has the ethylene linking in the $\alpha\beta$-position.

Trimethylhomogallaldehyde, $C_{11}H_{14}O_4$, b. p. 162—165°/10 mm., forms a *semicarbazone*, m. p. 188°. *Trimethylhomogallic acid*, $C_{11}H_{14}O_5$, m. p. 119—120°, forms a *methyl* ester, b. p. 172—182°/10 mm., D^{20} 1·153.

Trimethylgallaldehyde (3:4:5-*trimethoxybenzaldehyde*), $C_{10}H_{12}O_4$, m. p. 75°, b. p. 163—165°/10 mm., forms a *semicarbazone*, $C_{11}H_{15}O_4N_3$, m. p. 218°, and the *aldoxime*, $C_{10}H_{12}O_3\colon NOH$, m. p. 82—84°, b. p. 198—200°/10 mm. When heated with acetic anhydride, the aldoxime is converted into 3:4:5-*trimethoxybenzonitrile*, $C_{10}H_{11}O_3N$, m. p. 93°, b. p. 180—185°/10 mm., which on hydrolysis yields trimethoxybenzoic acid. G. Y.

Ethereal Oils, Material for the Investigation of. Roure-Bertrand Fils (*Chem. Zentr.*, 1908, i, 464—465; from *Wiss. indust. Ber. Roure-Bertrand Fils*, 1907, [2], **6**, 15—32).—Oil from Sandal Wood.—A yield of 3·8% oil, $[\alpha]_D + 47·07°$, D^{15} 0·9799, found to contain 0·4% ester and 44·1% alcohol calculated as linalyl acetate and linalool. Oil from Linaloe Seeds.—$[\alpha]_D + 1·5°$, after acetylation $[\alpha]_D - 3·2°$, D^{15} 0·8883, saponification number 29·2, 10·2% ester calculated as linalyl acetate, saponification number after acetylation 164·5, 51·6% alcohol calculated as linalool. Oil of Sage from Grasse.—Two samples examined, $[\alpha]_D$ + 6·13°, + 6·45°, D^{15} 0·915, 0·916, saponification number 13·4, after acetylation 53·7. Climate and soil are stated to influence the physical and chemical constants of this oil. Oil from *Tetranthera polyantha* var. *citrata.*—(1) *From the bark*: $[\alpha]_D$ + 20·5°, after acetylation + 8·77°, D^{15} 0·8673, saponification number 252·3; contains 8% citral, 10% citronellal, 56·5% alcohols, and 2·4% esters. (2) *From the leaves*: $[\alpha]_D$ − 15·5°, after acetylation − 4·3°, D^{15} 0·9013, saponification number after acetylation 104·7; contains 6% citral, 21·2% cineol, and 31·3% alcohols. (3) *From the fruit*: $[\alpha]_D$ + 12·7°, after acetylation + 10·2°, D^{15} 0·8872, saponification number after acetylation 172·5; contains 64% citral, 19·4% alcohols, and 2% esters. Oil from *Magnolia Kobus* D. C.—$[\alpha]_D$ − 1·33°, D^{15} 0·9432; contains about 15% citral and a small quantity of anethole and estragole (?). J. V. E.

Lævorotatory Component of Tarragon Oil. Maurice Daufresne and Flament (*Bull. Soc. chim.*, 1908, [iv], **3**, 656—658. Compare this vol., i, 19).—The lævorotation of the higher boiling fractions of tarragon oil is shown to be due to the presence of an unstable aldehyde, which on heating loses water and resinifies. It has already been suggested that the source of the *p*-methoxycinnamaldehyde noted as a constituent of the oil may be an aldehyde-alcohol of the constitution $OMe\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot CHO$ or

$$OMe\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot CHO$$

(*Bull. Soc. chim.*, 1908, [iv], 3, 330). T. A. H.

Congo-Copal and (White) Benguela-Copal. A. Engel (*Arch. Pharm.*, 1908, **246**, 293—305).—The portion of Congo-copal soluble in ether yields to sodium carbonate *Congocopalic acid*, $C_{19}H_{30}O_2$, m. p. 115—118° (48—50%), *a-Congocopaloresen* (5—6%), and an ethereal oil (3—4%); the residue, soluble in alcohol and ether, yields *Congocopalolic acid*, $C_{22}H_{334}O$, m. p. 108—110° (22%), and *β-Congocopaloresen*, m. p. 175—178° (12%); impurities and ash, 4—5%. For Benguela-copal the corresponding results are: *Bengucopalic acid*, $C_{19}H_{30}O_2$, m. p. 134—136° (43—45%), *a-Bengucopaloresen* (4—5%), ethereal oil (3—4%), *Bengucopalolic acid*, $C_{21}H_{32}O_3$, m. p. 114—116° (a lower homologue of Congocopalolic acid), 22%, and *β-Bengucopaloresen*, $C_{22}H_{36}O_2$, m. p. 192—196°. All these substances are amorphous. G. B.

Fagopyrum-Rutin. A. Wunderlich (*Arch. Pharm.*, 1908, **246**, 241—256).—The glucoside from the flowers of buckwheat (*Polygonum fagopyrum*) is identical with rutin from rue and with violaquercitrin (viola-rutin); it has the formula $C_{27}H_{30}O_{16},3H_2O$.

The quercetin trimethyl ether of Waliaschko (Abstr., 1904, i, 760), m. p. 154°, is hydrolysed by alcoholic potassium hydroxide to methylphloroglucinol and veratric acid; since hydroxyl groups in the ortho-position to the carbonyl groups are not directly methylated, this substance must be 1-hydroxy-3 : 3′ : 4′-trimethoxyflavanol. It yields on acetylation *diacetylquercetin trimethyl ether*, $C_{15}H_5O_7Me_3Ac_2$, m. p. 170—171°. The yellow substance, m. p. 240°, obtained by Waliaschko (*loc. cit.*) is *quercetin methyl ether*, $C_{15}H_9O_7Me$, and yields *tetra-acetylquercetin methyl ether*, $C_{15}H_5O_7MeAc_4$, m. p. 156—157°; this methyl ether differs from the three known quercetin monomethyl ethers. Acetylrutin, m. p. 114—116°, amorphous, probably contains nine acetyl groups, and would then have the composition $C_{27}H_{21}O_{16}Ac_9$. G. B.

Rhamnosides from Capparis spinosa and Globularia alypum. A. Wunderlich (*Arch. Pharm.*, 1908, **246**, 256—259).—The above rhamnosides are identical with rutin (compare preceding abstract). G. B.

Sakuranin, a New Glucoside from the Bark of Prunus Pseudo-Cerasus var. Sieboldi. Y. Asahina (*Arch. Pharm.*, 1908, **246**, 259—272).—*Sakuranin*, $C_{22}H_{24}O_{10},4H_2O$, is extracted by water from the bark of the Japanese cherry tree, and is obtained crystalline after precipitation of impurities by basic aluminium acetate solution. Crystallised from alcohol or ethyl acetate, it forms white needles, m. p. 210—212°, has a bitter taste and dissolves in alkalis with an intense yellow colour; it yields an amorphous *acetyl* derivative,

$$C_{22}H_{20}O_{10}Ac_4,$$

and a crystalline *benzoyl* derivative, $C_{22}H_{20}O_{10}Bz_4$, m. p. 227°. On hydrolysis, sakuranin yields equal molecules of dextrose and *sakuranetin*, $C_{16}H_{14}O_5$, crystals from ether or benzene, m. p. 150°. The latter substance contains one methoxyl group, absorbs bromine, and, when fused with potassium hydroxide, yields phloroglucinol, acetic and *p*-hydroxybenzoic acids. Sakuranin is physiologically inert, and does not produce glycosuria (like phloridzin). G. B.

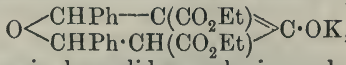
New Reduction Products of Artemisin. PASQUALE BERTOLO (*Gazzetta*, 1908, **38**, i, 554—559).—According to Rimini (*Soc. Chim. Roma*, Jan. 12, 1908), santonin and artemisin contain the same fundamental nucleus, the latter compound containing a hydroxyl group in place of a hydrogen atom of the former: santonin, $\cdot CO\cdot CH\vdots CMe\cdot$, artemisin, $\cdot CO\cdot C(OH)\vdots CMe\cdot$. The author points out that artemisin cannot contain a hydroxyl group, since it does not yield an acetyl or benzoyl derivative, and, on reduction with zinc dust and acetic acid, forms a dehydropinacone, artemisone (compare Bertolo and Ranfaldi, Abstr., 1905, i, 897). The formation of the latter compound, which may be regarded as an oxysantanone, indicates the presence in the molecule of a carbonyl group adjacent to a methylene group,

$$\cdot CO\cdot CH_2\cdot CMe\vdots.$$

The action of various reducing agents on artemisin has been studied, the results being as follows.

Reduction of artemisin with hydriodic acid and red phosphorus gives a good yield of a compound, m. p. 98—99°, crystallising from water in shining needles and somewhat resembling artemisic acid (compare Abstr., 1904, i, 177). Reduction with sodium amalgam gives an almost quantitative yield of an acid, m. p. 170°, of which the ethyl ester was prepared. Reduction by means of chromous hydroxide yields a small proportion of a substance which retains the lactonic linking and a ketonic carbonyl group, and has the same m. p., 170°, as santonin and, like the latter, turns yellow in the light and gives a violet coloration with sulphuric acid and ferric chloride; this substance is also obtained by reducing artemisin with ferrous hydroxide. Reduction of the hydrazone of artemisin with sodium amalgam gives an acid, m. p. 116°, which contains nitrogen. T. H. P.

Nearest Acid Derivatives of the Chlorophyllins. LEON MARCHLEWSKI (*Ber.*, 1908, **41**, 1858—1860. Compare Marchlewski and Schunck, Trans., 1900, **77**, 1080).—Polemical. A criticism of Tsvett's recent communication (this vol., i, 440). W. H. G.

Tetrahydropyrone Compounds. PAVEL PETRENKO-KRITSCHENKO and L. DEMENTEYEFF (*Ber.*, 1908, **41**, 1696—1697).—Ethyl 2:6-diphenyltetrahydropyrone-3:5-dicarboxylate in cold alcoholic solution reacts with concentrated alcoholic potassium hydroxide to form the *salt*,  $O{<}\begin{matrix}CHPh{-\!-}C(CO_2Et)\\ CHPh\cdot CH(CO_2Et)\end{matrix}{>}C\cdot OK$, whilst from the boiling solution cinnamic, benzylidenemalonic, and malonic acids have been isolated, and benzaldehyde detected by its odour. C. S.

Oxidation Products of Aconine. HEINRICH SCHULZE (*Arch. Pharm.*, 1908, **246**, 281—292. Compare Abstr., 1906, i, 599).—By the oxidation of aconine, ($C_{25}H_{41}O_9N$), with chromic acid, two substances,

$C_{24}H_{35}O_8N$ and $C_{24}H_{33}O_9N$, are formed, of which the former has basic and the latter both acid and basic properties; they appear to be an amino-alcohol and the corresponding amino-acid, and the acid has also been obtained by oxidation of the alcohol.

To the description of the base previously published, the following should be added. From analyses of the hydrochloride, the base has undoubtedly the formula $C_{24}H_{35}O_8N$, and the alternative formula $C_{24}H_{37}O_8N$, previously suggested, is now definitely excluded. The hydrochloride has $[\alpha]_D^{20}$ $+54\cdot37°$; the free base, m. p. 157—160°, its *sulphate*, and its *aurichloride* are all amorphous; the *hydriodide*, $C_{24}H_{35}O_8N,HI,3H_2O$, forms fine needles, m. p. 220—230° (decomp.). On acetylation, a crystalline *tetra-acetyl* derivative, m. p. 233° (decomp.), is formed, and, as the substance was previously shown to contain three methoxy-groups, seven of the eight oxygen atoms are thus accounted for, and the formula of the acetyl derivative may be written $C_{20}H_{19}O_5Ac_4(OMe)_3NMe$. The *aurichloride* of the acetyl derivative was also analysed.

Besides having one methoxy-group less, the base, $C_{24}H_{35}O_8N$, differs from aconine in reducing acid potassium permanganate, and also in forming a *methiodide*. The latter forms needles from alcohol, m. p. 222° (decomp.), and has the composition $C_{25}H_{38}O_8NI$. The only product which could be isolated on further oxidation of the base, $C_{24}H_{35}O_8N$, was a minute quantity of the hydrochloride of the undermentioned amino-acid.

The *amino-acid*, $C_{24}H_{33}O_9N$, is formed from aconine in larger quantity than the alcohol if much chromic acid is used. Its *hydrochloride* forms glassy plates and short prisms, soluble in water with acid reaction, of the composition $C_{20}H_{21}O_6(OMe)_3NMe,HCl,\frac{1}{2}H_2O$ (decomp. above 250°). The crystalline *barium* salt, $C_{48}H_{66}O_{18}N_2Ba,10H_2O$, and the crystalline *hydrochloride* of the amorphous *methyl* ester,

$$C_{19}H_{20}O_4(OMe)_3(NMe)\cdot CO_2Me,HCl,$$

m. p. 215—220° (decomp.), have also been analysed. G. B.

Carnine and Inosic Acid. FRANZ HAISER and FRANZ WENZEL (*Monatsh.*, 1908, **29**, 157—175. Compare Neuberg and Brahm, Abstr., 1907, i, 1097; Bauer, Abstr., 1907, i, 1098).—Carnine, originally obtained from meat extract by Weidel (Abstr., 1871, 716), is shown to be an approximately equal molecular mixture of hypoxanthine and a new substance, inosine, so named because it is evidently closely related to, and is probably derived from, the same parent substance as inosic acid. By slightly modifying the method of Weidel (*loc. cit.*), the authors have obtained about 5—6 grams each of carnine and inosic acid from one pound of fresh meat extract.

Inosine, $C_{10}H_{12}O_5N_4$, may be separated from carnine by repeated extraction with small quantities of water, in which it is fairly soluble, or by treating carnine with acetic anhydride and sodium acetate, when it is obtained in the form of an *acetate*, $C_{10}H_9O_2N_4(OAc)_3$ or $C_{20}H_{16}O_3N_8(OAc)_6$, crystallising in glistening, silky needles or rhomboidal plates, m. p. 236° (decomp.). Inosine crystallises in slender, silky needles, m. p. 215° (decomp.); $[\alpha]_D^{18} -49\cdot2°$; $[M]_D^{18} -131\cdot8°$ (in water); 100 c.c. of the saturated solution in water at 20° contains

1·615 grams of inosine; the *silver* salt, obtained as a gelatinous precipitate, is soluble in ammonia. Inosine is hydrolysed when boiled with dilute sulphuric acid, yielding hypoxanthine and a *pentose*, the *osazone* of which, $C_5H_8O_3(N\cdot NHPh)_2$, crystallises in microscopic, pale yellow needles, m. p. 163° (decomp.).

Hypoxanthine aurichloride, $C_5H_4ON_4,HAuCl_4$, crystallises in glistening, prismatic needles. W. H. G.

True Tannates of Quinine. II. PIETRO BIGINELLI (*Gazzetta*, 1908, **38**, i, 559—582. Compare Abstr., 1907, i, 955).—The author has prepared a number of true and false tannates of quinine and has studied their behaviour towards various reagents, the results obtained differing in some instances from those of Muraro (this vol., i, 451).

Hydrochloric acid acts on true tannates of quinine in the same way as dilute sulphuric acid, first displacing the tannic acid from its combination with quinine and then, as quinine salt, combining with the displaced tannic acid. Both the undissolved and dissolved portions represent pseudo-tannates, the nature of the former being independent of that of the true tannate employed; the dissolved false tannate, being, however, derived from quinine dihydrochloride, varies with the particular true tannate used.

In the action of tannic acid on quinine, several tannates of quinine are obtained, certain of them being formed in preference to the others according to the proportions of the components and the experimental conditions.

All the pseudo-tannates of quinine described in the various pharmacopœias are prepared from quinine sulphate or disulphate. They may be distinguished from the true tannates of quinine by the following methods: (1) 0·2—0·3 gram of the tannate is treated with a little moderately concentrated hydrochloric acid for a few minutes, after which 2—3 c.c. of water are added, and in a short time the acid decanted away. The yellow residue is treated with about 20 c.c. of water, with which it is shaken three or four times at intervals. If the residue dissolves completely, the original tannate is a true tannate of quinine, whilst, if there remains an undissolved residue, the compound examined is a pseudo-tannate derived from quinine sulphate or disulphate; (2) 0·2—0·3 gram of the tannate is treated with 2—3 c.c. of concentrated nitric acid, which is afterwards removed by heating on a water-bath. After cooling, the residue is treated with 20—30 c.c. of water and filtered, the filtrate being heated to 70° with a few drops of barium nitrate solution and then left. The gradual deposition of barium sulphate indicates a pseudo-tannate.

The following represent the compositions of the true tannates of quinine described by the author, the percentages of quinine present being indicated in brackets: $5C_{20}H_{24}O_2N_2,5C_{14}H_{10}O_9$ (50·15); $4C_{20}H_{24}O_2N_2,5C_{14}H_{10}O_9$ (44·59); $2C_{20}H_{24}O_2N_2,3C_{14}H_{10}O_9$ (40·14); $2C_{20}H_{24}O_2N_2,4C_{14}H_{10}O_9$ (33·47); $2C_{20}H_{24}O_2N_2,5C_{14}H_{10}O_9$ (28·70); $2C_{20}H_{24}O_2N_2,6C_{14}H_{10}O_9$ (25·11); $2C_{20}H_{24}O_2N_2,7C_{14}H_{10}O_9$ (22·32); T. H. P.

Cytisine. EMIL MAASS (*Ber.*, 1908, 41, 1635—1637).—The conclusion that one of the nitrogen atoms of cytisine is secondary, the other being tertiary, is supported by the preparation of *cytisine cytisinyldithiocarbamate*, $C_{11}H_{13}ON_2 \cdot CS \cdot SH,NH{:}C_{11}H_{13}ON$, from carbon disulphide; it forms a white powder, m. p. 197—198°, decomp. 200°. Hydrochloric acid regenerates cytisine and carbon disulphide; copper acetate, mercuric chloride, and silver nitrate give reddish-brown, white crystalline, and white, flocculent precipitates respectively.

Benzoylcytisine, $C_{18}H_{18}O_2N_2$, prepared by the Schotten-Baumann method, is difficult to purify; it forms prisms, m. p. 116°.

W. R.

Sparteine. XII. CHARLES MOUREU and AMAND VALEUR (*Bull. Soc. chim.*, 1908, [iv], 3, 674—678. Compare Scholtz, Abstr., 1906, i, 379).—Further results of work on the α and α'-sparteine methiodides (Abstr., 1905, i, 608, 609, 659) are given. The two isomerides may be separated by crystallisation from alcohol. When pure, the α'-methiodide has $[\alpha]_D$ $-47 \cdot 2°$, solubility in water 8% at 15°, and furnishes a hydriodide having $[\alpha]_D$ $-40 \cdot 32°$ in water, which, when heated, yields the same sparteine hydriodide as is obtained from the hydriodide of the α-isomeride (*loc. cit.*). Sparteine dihydriodide, $C_{15}H_{26}N_2,2HI,H_2O$, $[\alpha]_D$ $-15 \cdot 91°$, does not react with methyl iodide even when heated with it in a closed tube at 140—150°.

T. A. H.

Strychnos Alkaloids. I. New Method of Oxidising Brucine and Strychnine. HERMANN LEUCHS (*Ber.*, 1908, 41, 1711—1720).—When brucine and strychnine are oxidised with permanganate in acetone solution, 25% yields of crystalline acids, brucinonic acid,

$$C_{23}H_{24}O_8N_2$$

and strychninonic acid, $C_{21}H_{20}O_6N_2$, are formed respectively. These acids contain four atoms of oxygen more and two atoms of hydrogen less than the corresponding alkaloids, and it is suggested that they are formed by the rupture of an ethylene linking with the production of two carboxyl groups and at the same time the oxidation of a secondary alcoholic to a carbonyl group. The acids are thus regarded as ketonic dibasic acids. In addition to these acids, small amounts of dihydrobrucinonic acid, $C_{23}H_{26}O_8N_2$, and dihydrostrychninonic acid, $C_{21}H_{22}O_6N_2$, are also formed; these are probably the secondary alcohols corresponding with the ketonic acid.

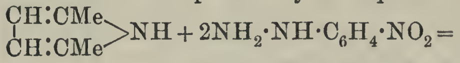
Brucinonic acid crystallises from water in colourless prisms containing H_2O, and has m. p. 178—183° (corr.), but when anhydrous sinters at 225° and melts at 266° (corr., decomp.); $[\alpha]_D^{20}$ $-48 \cdot 5°$. It dissolves readily in sodium carbonate solution, and behaves as a monobasic acid towards phenolphthalein or litmus. Solutions of its sodium salt yield precipitates with cupric sulphate, ferric chloride, silver nitrate, and lead acetate. The *monoethyl* ester, $C_{25}H_{28}O_8N_2$, obtained by the Fischer-Speyer method, crystallises from absolute alcohol in colourless prisms, m. p. 132°, or from glacial acetic acid in prisms, m. p. 161—163°.

Dihydrobrucinonic acid crystallises from hot glacial acetic acid in minute needles; it is lævorotatory in concentrated solution, but dextrorotatory in more dilute solution.

Strychninonic acid crystallises from hot water in colourless prisms containing $2H_2O$. When anhydrous, it melts and decomposes at 265—267° (corr.), and has $[\alpha]_D^{20}$ $-43{\cdot}3°$. *Dihydrostrychninonic acid* crystallises in rectangular plates, decomposes at about 315° (corr.), and has $[\alpha]_D^{20}$ $+4{\cdot}3°$ in 3·5% solution. The acids are not poisonous.

J. J. S.

A Transformation of Dimethylpyrrole. Angelo Angeli and Guerriero Marchetti (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 485—486. Compare this vol., i, 207).—The interaction of ethyl formate and 2 : 5-dimethylpyrrole yields a mixture which, with *p*-nitrophenylhydrazine, gives a small quantity of a hydrazone, which is probably acetonylacetone-*p*-nitrophenylhydrazone. This compound, which is also obtained when 2 : 5-dimethylpyrrole is treated with *p*-nitrophenylhydrazine, is formed by the opening of the pyrrole ring in the manner expressed by the equation:



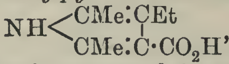
$$\begin{matrix}CH{:}CMe\\ | \\ CH{:}CMe\end{matrix}\!\!>NH + 2NH_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2 =$$

$$NO_2{\cdot}C_6H_4{\cdot}N_2H{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}N_2H{\cdot}C_6H_4{\cdot}NO_2.$$

The hydrazines are hence able to convert dimethylpyrrole into ketohydrazones in the same way as hydroxylamine. T. H. P.

Synthesis of Ethyl 2 : 5-Dimethyl-3-ethylpyrrole-4-carboxylate. Georg Korschun (*Bull. Soc. chim.*, 1908, [iv], 3, 593—595. Compare Abstr., 1905, i, 373).—A continuation of work on the synthesis of similar esters by Hantzsch's method (Abstr., 1890, i, 1155).

Ethyl 2 : 5-*dimethyl*-3-*ethylpyrrole*-4-*carboxylate*,

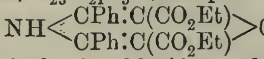


$$NH<\begin{matrix}CMe{:}CEt\\ \quad\ \ |\\ CMe{:}C{\cdot}CO_2H\end{matrix},$$

m. p. 74—75°, could not be prepared by treating a mixture of ethyl acetoacetate and methyl α-chloropropyl ketone with ammonia, but a yield of about 27% of the theoretical was eventually obtained by the replacement of ethyl acetoacetate by ethyl β-aminocrotonate. The ester is difficult to purify by recrystallisation, and recourse was had to treating the crude product with a boiling solution of potassium hydroxide in methyl alcohol, which attacks the associated impurities, but has no action on the pyrrole ester. The latter was finally obtained in colourless, brilliant, bulky crystals from dilute methyl alcohol.

T. A. H.

Condensation of Acetonedicarboxylic Esters with Aldehydes under the Influence of Ammonia and Amines. III. Pavel Petrenko-Kritschenko and W. Petroff (*Ber.*, 1908, 41, 1692—1695. Compare Abstr., 1906, i, 452; 1907, i, 708).—The substances described previously as the nitrosoamines of the esters of 2 : 6-diphenylpiperidone-3 : 5-dicarboxylic acid and its *N*-methyl homologue are in reality the nitrites, since the bases are liberated by ammonium hydroxide in the cold.

The piperidone structure of the condensation products of ethyl acetonedicarboxylate with aldehydes has been proved by oxidising ethyl 2 : 6-diphenylpiperidone-3 : 5-dicarboxylate with chromic and acetic acids, whereby a *substance*, $C_{23}H_{21}O_5N$, m. p. 195°, is obtained, which receives the constitution  $NH\Big<\begin{matrix}CPh{:}C(CO_2Et)\\ CPh{:}C(CO_2Et)\end{matrix}\Big>CO$, because it does not give a coloration with ferric chloride, and is hydrolysed without fission by concentrated boiling alcoholic potassium hydroxide, yielding the *acid*, $C_{19}H_{13}O_5N$, m. p. 258° (decomp.).

The piperidone bases in benzene solution form salts with mineral acids which are insoluble in water. When, however, an alcoholic solution of the base is treated with a mineral acid, excepting nitric, the salts are not precipitated by the addition of water; from the solutions, ammonium hydroxide and platinum tetrachloride precipitate the unchanged bases and the platinichlorides respectively. The nitrites and nitrates, however, do not exist in the soluble forms, and are precipitated by the addition of these acids to the solutions of the salts. The *nitrate* of ethyl diphenylpiperidonedicarboxylate, $C_{23}H_{25}O_5N,HNO_3$, m. p. 154—157°, has been prepared in this way.

C. S.

Decomposition of 3-Methyl 2-Hydrogen Quinolinate. ALFRED KIRPAL (*Monatsh.*, 1908, **29**, 227—234. Compare Abstr., 1907, i, 722).—It has been proved that the compound obtained as a by-product in the preparation of 2-methyl 3-hydrogen quinolinate by the action of methyl alcohol on the anhydride of the acid is 3-methyl 2-hydrogen quinolinate (Abstr., 1906, i, 697). The ammonium quinolinamate derived from the ester is converted by the action of alkaline hypobromite into a compound which must be 3-aminopicolinic acid, since, when heated above its melting point, it liberates carbon dioxide, yielding 3-aminopyridine (compare Pollak, Abstr., 1895, i, 391).

The quinolinamate is also converted through the diazo-compound into a substance which must be 3-hydroxypicolinic acid, for it yields 3-hydroxypyridine on distillation.

3-*Aminopicolinic acid*, $2NH_2{\cdot}C_5H_3N{\cdot}CO_2H,H_2O$, crystallises in faintly coloured plates, m. p. 210° (decomp.).

3-*Hydroxypicolinic acid*, $OH{\cdot}C_5H_3N{\cdot}CO_2H$, crystallises in colourless prisms or small, triangular plates, m. p. 215°. W. H. G.

Nitration of Quinoline and its Mononitro-derivatives. II. ADOLF KAUFMANN and HANS HÜSSY (*Ber.*, 1908, **41**, 1735—1742. Compare Abstr., 1906, i, 984).—Quinoline when nitrated yields a mixture of equal amounts of 5- and 8-nitroquinolines. The 5-nitro-derivative on further nitration yields 5 : 7-dinitro-, and the 8-mononitro- yields 6 : 8-dinitro-quinoline (Claus and Hartmann's 5 : 8-dinitroquinoline). 6-Nitroquinoline yields a mixture of 5 : 6- and 6 : 8-dinitroquinolines, and 7-nitroquinoline yields a mixture of the 5 : 7- and 7 : 8-dinitro-compounds.

The 6 : 7-dinitroquinoline cannot be obtained by direct nitration or by synthesis.

6 : 8-Dinitroquinoline is obtained free from the isomeric 5 : 6-compound when 6-nitroquinoline is added gradually to a mixture of sulphur trioxide and concentrated nitric acid, and the temperature allowed to rise gradually to 100° while the mixture is stirred. The constitution of the dinitroquinolines has been established by their syntheses from substituted anilines by Skraup's method, using either arsenic or picric acid as oxidising agent.

The melting points are 5 : 7, 180°; 5 : 6, 185°; 7 : 8, 221—223°. The 5 : 7-dinitro-compound dissolves in aqueous sodium hydroxide, yielding a red solution, whereas the 7 : 8-compound yields a yellow solution. The dinitro-compounds do not combine directly with methyl iodide; the 5 : 6-derivative, however, combines with methyl sulphate, and from this sulphate a *methiodide*, $C_9H_5O_4N_3$,MeI, can be obtained by double decomposition. It crystallises from water in brilliant dark red plates, and decomposes at 125—126°. J. J. S.

Fixation of Aromatic Amines on Vinyl Ketones. 4-Alkylquinolines. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 658—667).—The authors have studied the condensation of aromatic amines with vinyl ketones. In absence of water, the action of aniline on the β-chloro-ketones gives rise to the formation of 4-alkylquinolines. This is a general method of synthesis, and gives pure compounds, although the yield is not very good.

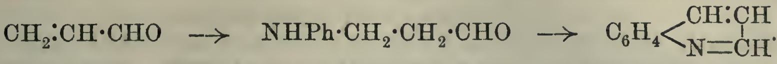
β-Anilinoethyl ethyl ketone, $NHPh{\cdot}C_2H_4{\cdot}COEt$, is obtained by heating a mixture of aniline, water, and ethyl chloroethyl ketone on the water-bath, and crystallises from ether in plates, m. p. 55·5°. The *semicarbazone* has m. p. 130° (decomp.), and the *phenylcarbamide*, m. p. 76—77°. *β-Anilinoethyl propyl ketone*, $NHPh{\cdot}C_2H_4{\cdot}COPr^{a}$, prepared from chloroethyl propyl ketone, separates from alcohol in pale yellow leaflets, m. p. 60°. The *phenylcarbamide* has m. p. 107—108°. *β-Methylanilinoethyl ethyl ketone*, $NPhMe{\cdot}C_2H_4{\cdot}COEt$, has b. p. 164°/15 mm.; the *semicarbazone* has m. p. 163°, and the *picrate*, m. p. 110°. *β-2-Carboxyanilinoethyl ethyl ketone*,

$$CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}C_2H_4{\cdot}COEt,$$

has m. p. 106°.

4-*Ethylquinoline* (see following abstract) is obtained by heating on the water-bath a mixture of aniline (2 mols.), aniline hydrochloride (1 mol.), ethyl β-chloroethyl ketone (1 mol.), and an amount of absolute alcohol equal to the weight of the aniline hydrochloride. β-Anilinoethyl ethyl ketone is an intermediate product in this reaction, for it yields 4-ethylquinoline when heated with aniline hydrochloride. J. C. C.

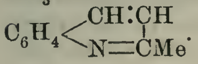
4-Alkylquinolines. Mechanism of the Reactions of Skraup and of Doebner and Miller. EDMOND E. BLAISE and M. MAIRE (*Bull. Soc. chim.*, 1908, [iv], 3, 667—674).—In view of the light thrown on the mechanism of the formation of quinolines (see preceding abstract), the authors consider that both Skraup's reaction and that due to Doebner and Miller can be explained in the same way. Skraup's reaction is to be regarded as (1) formation of an acraldehyde; (2) fixation of a mol. of aniline on the double linking, and (3) ring formation by elimination of water and loss of two atoms of hydrogen, thus:



$$CH_2{:}CH{\cdot}CHO \longrightarrow NHPh{\cdot}CH_2{\cdot}CH_2{\cdot}CHO \longrightarrow C_6H_4{<}\begin{matrix}CH{:}CH\\ N{=}CH\end{matrix}.$$

In the case of Doebner and Miller's reaction, the mechanism is:

$2CH_3{\cdot}CH{:}NPh = NHPh{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}NPh$ or $2CH_3{\cdot}CHO \longrightarrow CH_3{\cdot}CH{:}CH{\cdot}CHO + 2NH_2Ph \longrightarrow NHPh{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}NPh \longrightarrow$



$$C_6H_4{<}\begin{matrix}CH{:}CH\\ N{=}CMe\end{matrix}.$$

4-*Ethylquinoline* (preceding abstract) has b. p. 134°/9 mm. The following salts are described: *picrate*, canary-yellow needles, m. p. 192° (decomp.), *dichromate*, brown needles, m. p. 94°, *platinichloride*, orange crystals, m. p. 208° (decomp.), *aurichloride*, yellow needles, m. p. 156°, *mercurichloride*, needles, m. p. 161°, *cadmiobromide*, needles, m. p. 204°, *methiodide-di-iodide*, brown crystals, m. p. 120—121°. On oxidation with chromic acid, 4-ethylquinoline yields cinchoninic acid.

4-Propylquinoline (Koenigs, Abstr., 1899, i, 75), prepared from aniline and β-chloroethyl propyl ketone, has b. p. 159°/16 mm.; the picrate, m. p. 204°, the platinichloride, m. p. 198° (decomp.), the *mercurichloride*, m. p. 148°, the *cadmiobromide*, m. p. 148°. J. C. C.

Constitution of the Compounds of Tetramethyldiaminobenzhydrol with some Methylenic Derivatives. ROBERT FOSSE (*Compt. rend.*, 1908, **146**, 1039—1042. Compare Abstr., 1907, i, 414).—The condensation of this alcohol with methylene compounds can be most simply represented thus: $CH(C_6H_4{\cdot}NMe_2)_2{\cdot}OH + HCHXY = CH(C_6H_4{\cdot}NMe_2)_2{\cdot}CHXY + H_2O$. But the fact that all the compounds produced, when treated with dimethylamine in the presence of acetic acid, regenerate the methylene compound and give the leuco-base of crystal-violet suggests that the combination occurs through the oxygen atom, thus: $CH(C_6H_4{\cdot}NMe_2)_2{\cdot}OH + HO{\cdot}CMe{:}CH{\cdot}CO_2Et = CH(C_6H_4{\cdot}NMe_2)_2{\cdot}O{\cdot}CMe{:}CH{\cdot}CO_2Et$. From the behaviour of the condensation compounds, however, the author concludes that in neutral or alkaline solution they have the constitution first suggested. Thus ethyl tetramethyldiaminobenzhydrylacetylacetate, $C_{23}H_{30}O_3N_2$, must have the constitution $CH(C_6H_4{\cdot}NMe_2)_2{\cdot}CH(COMe){\cdot}CO_2Et$, since it forms an *oxime*, crystalline needles, m. p. 205°, and on hydrolysis loses carbon dioxide, giving a new ketone, pp-*tetramethyldiaminobenzhydrylpropanone*, $CH(C_6H_4{\cdot}NMe_2)_2{\cdot}CH_2{\cdot}COMe$, needles, m. p. 110°, which forms an *oxime*, m. p. 136—137°, a *semicarbazone*, m. p. 185° (decomp.), a *dihydrochloride*, and a *platinichloride*. As ethyl tetramethyldiaminobenzhydrylbenzoylacetate, $C_{28}H_{32}O_3N_2$, on hydrolysis loses carbon dioxide, giving *tetramethyldiaminobenzhydrylacetophenone*,

$$CH(C_6H_4{\cdot}NMe_2)_2{\cdot}CH_2{\cdot}COPh,$$

fine brilliant needles, m. p. 145°, which forms an *oxime* and a *platinichloride*, whilst, when treated with concentrated alcoholic potash, it undergoes simultaneously both "acid" and "ketone" hydrolysis, giving benzoic and tetramethyldiaminobenzhydrylacetic acids, tetramethyldiaminobenzhydrylacetophenone, carbon dioxide, and alcohol, its constitution must be represented by the formula

$$CH(C_6H_4\cdot NMe_2)_2\cdot CH(COPh)\cdot CO_2Et.$$

Similarly, tetramethyldiaminobenzhydrylacetylacetone should be represented by $CH(C_6H_4\cdot NMe_2)_2\cdot CH(COMe)_2$, since alcoholic potash transforms it into potassium acetate and the substituted propanone described above. Again, alcoholic potash converts tetramethyldiaminobenzhydrylbenzoylacetone into a mixture of the two mono-ketones, tetramethyldiaminobenzhydrylacetone and tetramethyldiaminobenzhydrylacetophenone, and therefore $CH(C_6H_4\cdot NMe_2)_2\cdot CH(COMe)\cdot COPh$ must be the formula of the diketone.

The oxide formula is inapplicable to tetramethyldiaminobenzhydrylmalonic acid and its derivatives, which must have the constitution $CH(C_6H_4\cdot NMe_2)_2\cdot CH(CO_2H)_2$. This acid can be prepared from the ethyl ester or it can be obtained directly. When malonic acid reacts with the hydrol, there is formed either tetramethyldiaminobenzhydrylacetic acid (Abstr., 1907, i, 136) or the substituted malonic acid, thus:

$$CH(C_6H_4\cdot NMe_2)_2\cdot OH + H\cdot CH(CO_2H)_2 = H_2O + CH(C_6H_4\cdot NMe_2)_2\cdot CH(CO_2H)_2.$$

E. H.

Constitution of the Methylene Derivatives of Tetramethyldiaminodiphenylmethane. Replacement of Hydroxyl in Michler's Carbinol by the Alkylmethylene Radicle. Robert Fosse (*Compt. rend.*, 1908, **146**, 1277—1280. Compare preceding abstract).—The author has extended his work on the condensation of tetramethyldiaminobenzhydrol. The constitution of the methylene derivatives described in the present paper is not in accord with Weil's ketonic formula (Abstr., 1894, i, 419) for the carbinol. The compounds have the constitution $(C_6H_4\cdot NMe_2)_2CH\cdot CXYR$, and give a colourless solution with cold acetic acid, which becomes intensely blue on heating. They are decomposed in acetic acid solution in presence of dimethylaniline into the methylenic constituent and the leuco-base of crystal-violet. *Methyl tetramethyldiaminobenzhydrylmethylacetoacetate*, $CH(C_6H_4\cdot NMe_2)_2\cdot CMeAc\cdot CO_2Me$, has m. p. 113—114°. Under the influence of semicarbazide, it yields methyl methylacetoacetate and *tetramethyldiaminobenzhydrylsemicarbazide*,

$$CH(C_6H_4\cdot NMe_2)_2\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

m. p. 185—187°, and when treated with alcoholic potash furnishes *a-tetramethyldiaminobenzhydrylpropionic acid*,

$$CH(C_6H_4\cdot NMe_2)_2\cdot CHMe\cdot CO_2H,$$

sintering at 170°, m. p. 190°, the *ethyl* ester of which has m. p. 103—104°, and *methyl tetramethyldiaminodiphenyl*iso*propyl ketone*,

$$CH(C_6H_4\cdot NMe_2)_2\cdot CHMe\cdot COMe,$$

m. p. 144—145°; the *semicarbazone* sinters at 200°, m. p. 215—216° (decomp.). *Tetramethyldiaminobenzhydrylmethylacetylacetone*,

$$CH(C_6H_4\cdot NMe_2)_2\cdot CMe(COMe)_2,$$

has m. p. 140—143°. With alcoholic potash, it gives methyl tetramethyldiaminodiphenyl*iso*propyl ketone.

J. C. C.

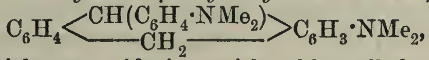
Amino-derivatives of *o*-Dibenzoylbenzene. ALFRED GUYOT and P. PIGNET (*Compt. rend.*, 1908, **146**, 984—987. Compare Guyot and Catel, Abstr., 1905, i, 226, 516, 540; 1906, i, 761; 1907, i, 76).—p-*Dimethylaminobenzoyl*-2-p-*dimethylaminobenzylbenzene*,

$$NMe_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2,$$

m. p. 133°, prepared by the condensation of dimethylaniline with *p*-dimethylaminobenzylbenzoyl chloride in the presence of aluminium chloride, forms pale yellow needles, and does not yield condensation products with hydrazine, phenylhydrazine, hydroxylamine, or semicarbazide; it forms a *trinitro*-derivative, $C_{24}H_{23}O_7N_5$, m. p. 174°, crystallising in brilliant yellow prisms; it is reduced by sodium amalgam to *tetramethyl*-p-*diaminobenzylbenzhydrol*,

$$NMe_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2,$$

colourless prisms, m. p. 98°, which on further reduction yields 1 : 2-*di*-p-*dimethylaminobenzylbenzene*, $C_6H_4(CH_2\cdot C_6H_4\cdot NMe_2)_2$, m. p. 90°. When tetramethyldiaminobenzylbenzhydrol is mixed with concentrated sulphuric acid, it loses H_2O and forms an anthracene derivative, 2-*dimethylamino*-9-p-*dimethylaminophenyldihydroanthracene*,



$$C_6H_4{<}\begin{matrix}CH(C_6H_4\cdot NMe_2)\\CH_2\end{matrix}{>}C_6H_3\cdot NMe_2,$$

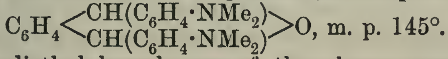
m. p. 168°, which on oxidation with chloranil loses H_2 and is converted into 2-*dimethylamino*-9-p-*dimethylaminophenylanthracene*, $C_{24}H_{24}N_2$, m. p. 184°. 1 : 2-*Di*-p-*dimethylaminobenzoylbenzene*,

$$C_6H_4(CO\cdot C_6H_4\cdot NMe_2)_2,$$

m. p. 207°, obtained as pale yellow prisms by the oxidising action of chloranil on *p*-dimethylaminobenzoyl-2-*p*-dimethylaminobenzylbenzene, yields a mono*phenylhydrazone*, $C_{30}H_{30}ON_4$, m. p. 194°, a *dioxime*, $C_{24}H_{26}O_2N_4$, m. p. 230°, and a *phthalazine*, $C_{24}H_{24}N_4$, m. p. 281°; it yields on reduction 1 : 2-*di*-p-*dimethylaminohydroxybenzylbenzene*,

$$C_6H_4[CH(OH)\cdot C_6H_4\cdot NMe_2]_2,$$

m. p. 124°, which loses H_2O by the action of phosphoryl chloride and is converted into 1 : 2-p-*dimethylaminophenyl*-1 : 2-*dihydro*iso*benzofuran*,



$C_6H_4{<}\begin{matrix}CH(C_6H_4\cdot NMe_2)\\CH(C_6H_4\cdot NMe_2)\end{matrix}{>}O$, m. p. 145°.

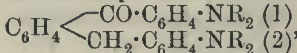
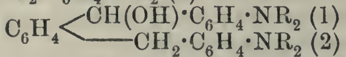
The diethyl homologues of the above compounds have also been prepared: p-*diethylaminobenzoyl*-2-p-*dimethylaminobenzylbenzene*,

$$NEt_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2,$$

m. p. 104°, and *trinitro*-derivative, $C_{26}H_{27}O_7N_5$, m. p. 125°; p-*diethylamino*-p-*dimethylaminobenzylbenzhydrol*,

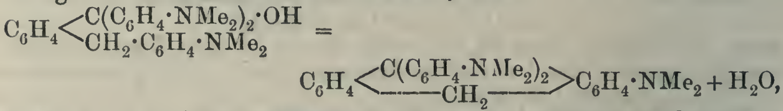
$$NEt_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2,$$

highly refractive, colourless crystals, m. p. 73°; 1-p-*diethylaminobenzyl*-2-p-*dimethylaminobenzylbenzene*, $NEt_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2$ m. p. 57°; the *dihydroanthracene* derivative, $C_{26}H_{30}N_2$, m. p. 113 the *anthracene* derivative, $C_{26}H_{28}N_2$, m. p. 132°; 1-p-*diethylaminobenzoyl*-2-p-*dimethylaminobenzoylbenzene*, $NEt_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot NMe_2$, m. p. 110°, and its *phthalazine*, $C_{26}H_{28}N_4$, m. p. 189°, and *phenylhydrazone*, $C_{32}H_{34}ON_4$, m. p. 170°. M. A. W.

Some *o*-Benzylated Dyes from Triphenylmethane. ALFRED GUYOT and P. PIGNET (*Compt. rend.*, 1908, **146**, 1043—1045).—The stability towards alkalis conferred on dyes of the type of malachite-green by substituting groups in the ortho-position to the methane carbon atom is usually explained by a steric protection by these groups. On this hypothesis, it would be expected that groups of higher molecular weight would have a proportionally greater effect, and it has been found, in fact, that the benzyl group has a protective action of the same order as the sulphonic group when substituted in the ortho-position. The tetra-alkyldiamino-*o*-benzoylbenzylbenzenes,  $C_6H_4{<}\begin{matrix}CO\cdot C_6H_4\cdot NR_2\ (1)\\ CH_2\cdot C_6H_4\cdot NR_2\ (2)\end{matrix}$, and the tetra-alkyldiamino-*o*-benzylbenzhydrols,  $C_6H_4{<}\begin{matrix}CH(OH)\cdot C_6H_4\cdot NR_2\ (1)\\ CH_2\cdot C_6H_4\cdot NR_2\ (2)\end{matrix}$ (preceding abstract), readily condense with various amines, giving *o*-benzylated malachite-greens or their leuco-derivatives. Thus dimethylaniline in the presence of phosphoryl chloride reacts with tetramethyldiamino-*o*-benzoylbenzylbenzene, giving *o-dimethylaminobenzylphenyltetramethyldiaminodiphenylcarbinol*, $NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot C(C_6H_4\cdot NMe_2)_2\cdot OH$, which can be isolated in the form of small, reddish-brown crystals of the *zincichloride*, $C_{32}H_{36}N_3Cl_3Zn$. The dye also forms a double *nitrate* with potassium, $C_{32}H_{36}O_6N_5K$, beautiful crystals having a coppery reflex, and a similar *sodium salt*. The *leuco-base*, $C_{32}H_{37}N_3$, fine white needles, m. p. 162°, is easily obtained by reducing the dye with zinc and hydrochloric acid, or by the direct condensation of dimethylaniline with tetramethyldiamino-*o*-benzylbenzhydrol,

$$NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot NMe_2.$$

This dye, like all the amido-dyes derived from triphenylmethane, dissolves in concentrated sulphuric acid with an orange-red coloration; in this instance, however, the liquid is rapidly decolorised, owing to an intramolecular condensation, thus:



$$C_6H_4{<}\begin{matrix}C(C_6H_4\cdot NMe_2)_2\cdot OH\\ CH_2\cdot C_6H_4\cdot NMe_2\end{matrix} = C_6H_4{<}\begin{matrix}C(C_6H_4\cdot NMe_2)_2\\ CH_2\end{matrix}{>}C_6H_4\cdot NMe_2 + H_2O,$$

giving 2 : 13 : 13′-*hexamethyltriamino*-9 : 9-*diphenyldihydroanthracene*, a white, crystalline powder, m. p. 175°, giving colourless solutions in dilute mineral acids.

By using diethylaniline in place of the methyl derivative, the homologue of the above dye is obtained, and can be isolated in the form of the *zincichloride*, $C_{34}H_{40}Cl_3N_3Zn$, and the double *nitrates* with *sodium* and *potassium*, $C_{34}H_{40}O_6N_5Na$ and $C_{34}H_{40}O_6N_5K$. The *leuco-base*, $C_{34}H_{41}N_3$, has m. m. 107°.

When *o*-dimethylaminobenzyldiethylaminobenzoylbenzene is similarly condensed with diethylaniline, an *o*-dimethylaminobenzyl derivative in the form of a brilliant green is produced. This gives the double *nitrates* $C_{36}H_{41}O_6N_5K$ with *potassium*, and $C_{36}H_{41}O_6N_5Na$ with *sodium*, and a *leuco*-derivative, $C_{36}H_{45}N_3$, m. p. 118°. E. H.

Striking Fluorescence Phenomena in Picryl Compounds.

HEINRICH LEY [in part F. MÜLLER and P. KRAFFT] (*Ber.*, 1908, 41, 1637—1644).—It has already been noted that $\alpha\beta$-diphenyl-γ-benzylhydroxyamidine picrate and analogous compounds (Abstr., 1901, i,

759) are strongly fluorescent, a result in direct contradiction to the generalisation that the introduction of nitro-groups depresses the fluorescence. The same phenomenon is observed with the picryl compounds of diguanidine, guanylformamidide, and diformamidide. Ley and Müller have likewise shown that abnormally coloured and very stable salts are given by analogous amidides (Abstr., 1907, i, 730), and the fluorescence may be explained in a similar way, the supplementary valencies of the picryl radicle acting on a basic group, $:NPh$ for example.

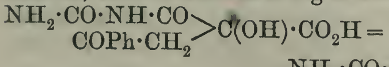
Whereas the free diphenylbenzylhydroxyamidine has only a shallow band, and picryl chloride no absorption in the ultra-violet, yet the picryl derivative has two well-defined bands, one in the greenish-violet and the other in the ultra-violet. The fluorescent spectrum has also a broad band in the visible spectrum, but no rays could be detected in the ultra-violet, a result in partial harmony with the conclusion drawn by Stark and Meyer that there is a parallelism between the absorption and fluorescent spectra (Abstr., 1907, ii, 418; compare, also, ii, 147). The results are not in harmony with Hewitt's theory (Abstr., 1900, ii, 318), but may be explained by Stark's (this vol., ii, 138) or by Collie and Baly's oscillation hypothesis (Trans., 1905, **87**, 1332).

The fluorescence diminishes in the order of the following solvents: ethyl acetate, chloroform, benzene, carbon tetrachloride, acetone, carbon disulphide, amyl alcohol, ethyl alcohol, methyl alcohol.

The dark orange picryl-$\alpha\beta$-diphenyl-γ-benzylhydroxyamidine crystallises from a mixture of chloroform and light petroleum in yellow crystals, which are composed of 13 or 14 mols. of amidine and 1 mol. of solvent, m. p. 110°.

Picrylphenyldiguanide, $NH:C(NHPh)\cdot N[C_6H_2(NO_2)_3]\cdot C(NH_2):NH$, obtained from the hydrochloride, picryl chloride, and sodium ethoxide, forms glistening, brownish-red crystals, m. p. 205°, and has a yellowish-green fluorescence in acetone. Neither diguanide nor β-diphenyl diguanide gives fluorescent picryl derivatives, but *picryl-$\beta\delta\epsilon$-triphenylguanylamidide*, $NH:CPh\cdot N[C_6H_2(NO_2)_3]\cdot C(NHPh):NPh$, red needles, m. p. 182°, gives intense yellow, fluorescent solutions. W. R.

Phenacyl-dialuric Acid, -tartronuric Acid, and -*iso*hydantoic Acid. Otto Kühling (*Ber.*, 1908, **41**, 1658—1664).—The compound obtained in the attempt to benzoylate phenacyldialuric acid by the Schotten-Baumann method, and previously described as phenacylalanturic acid (Abstr., 1905, i, 944), is now shown to be phenacyl*iso*hydantoic acid, $NH_2\cdot CO\cdot NH\cdot CO\cdot CH(OH)\cdot CH_2\cdot COPh$, since it is obtained by boiling solutions of phenacyltartronuric acid in water or acetone, carbon dioxide being liberated, thus:



$$\begin{matrix}NH_2\cdot CO\cdot NH\cdot CO \\ COPh\cdot CH_2\end{matrix}>C(OH)\cdot CO_2H = NH_2\cdot CO\cdot NH\cdot CO\cdot CH(OH)\cdot CH_2\cdot COPh + CO_2.$$

Phenacyltartronuric acid is obtained by treating phenacyldialuric acid with dilute aqueous sodium carbonate solution; it crystallises in microscopic needles, m. p. 144—145° (decomp.). The *lead* salt,

$(C_{12}H_{11}O_6N_2)_2Pb$,

needle-shaped prisms, *silver* salt, $C_{12}H_{11}O_6N_2Ag$, a thick, gelatinous precipitate, and *sodium* salt, $C_{12}H_{10}O_6N_2Na_2$, a white, flocculent precipitate, were prepared and analysed.

*Phenacyl*iso*hydantoic acid* crystallises in concentrically grouped leaflets, m. p. 161—162° (decomp.). W. H. G.

Some Methods of Preparation of Triazans. GUIDO GOLDSCHMIEDT (*Ber.*, 1908, **41**, 1862—1864).—Polemical. The compound obtained by Michaelis (this vol., i, 471) from *as*-phenylbenzylhydrazine by various methods of preparation and supposed to be diphenyldibenzyltriazan is undoubtedly phenylbenzylbenzylidenehydrazone, a compound always present in old specimens of *as*-phenylbenzylhydrazine (compare Ofner, Abstr., 1904, i, 818 ; Milrath, following abstract).

The compound described by Michaelis (*loc. cit.*) as triphenylbenzyltriazan is probably diphenylbenzylidenehydrazone. W. H. G.

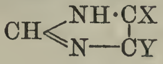
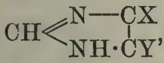
Conditions of Formation of Phenylsemicarbazide and of Acetylphenylhydrazine. HUGO MILRATH (*Monatsh.*, 1908, **29**, 337—350).—The author has repeated Jaffé's work on the production of phenylsemicarbazide from carbamide, phenylhydrazine, and acetic acid (Abstr., 1897, ii, 575), and finds that either acetylphenylhydrazine or a mixture of this with phenylsemicarbazide is obtained in this reaction. For the exclusive formation of the latter, the transformation of carbamide into ammonium cyanate is necessary, as is also a high temperature, a long period of heating, and an increased concentration of carbamide. Acetylphenylhydrazine is largely formed by warming equal molecular quantities of phenylhydrazine and 7% acetic acid on the water-bath. Dog's and cat's urine, rich in carbamide, furnish phenylsemicarbazide only when warmed for four to five hours with phenylhydrazine and acetic acid ; when normal human urine is used, the mixture must be warmed for at least five hours. J. C. C.

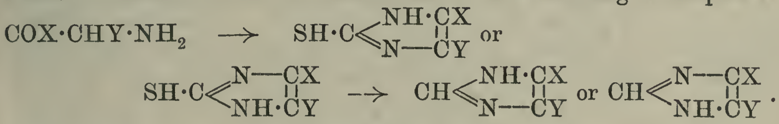
Condensation of Gallocyanin Dyes with Amino-compounds. EUGÈNE GRANDMOUGIN and ERNST BODMER (*J. pr. Chem.*, 1908, [ii], **77**, 498—510. Compare Abstr., 1907, i, 355).—It was shown previously (this vol., i, 289) that pruneanilide and correinanilide are formed by condensation of prune and correin with aniline. Details are now given of the preparation of similar condensation products of prune with *m*- and *p*-aminobenzoic acids, *o*-, *m*-, and *p*-nitroanilines, methylaniline, *p*-phenylenediamine, and benzidine. The *substance* obtained by condensation of prune with sulphanilic acid is not identical with the product of the sulphonation of pruneanilide. *Prune sulphate*, $C_{16}H_{14}O_5N_2,H_2SO_4$, olive leaflets, and *picrate*, $C_{16}H_{14}O_5N_2,C_6H_3O_7N_3$, green leaflets, were analysed.

Cœlestin-blue B (correin RR) forms a green, crystalline *picrate*, $C_{17}H_{17}O_4N_3,C_6H_3O_7N_3$. The condensation of the base with *o*-, *m*-, and *p*-aminobenzoic acids, *m*- and *p*-nitroanilines, and diethyl-*p*-phenylenediamine is described. G. Y.

Hydantoin and the Isomerism of the Methylhydantoins. Carl D. Harries (*Annalen*, 1908, 361, 69—72).—The *iso*-ε-methylhydantoin described by Harries and Weiss (Abstr., 1903, i, 738) has now been found to be a mixture of ε-methylhydantoin and smaller amounts of another substance, which has not been completely separated; on repeated recrystallisation, fractions, m. p. 147—156° and m. p. 178°, were obtained.

When heated with alcoholic ammonia at 100°, ethyl hydantoate yields hydantoin, and not aminoacetamide as previously stated (*loc. cit.*). G. Y.

Tautomerism in the Iminazole Series. Siegmund Gabriel (*Ber.*, 1908, 41, 1926—1928).—The virtual tautomerism of the benziminazoles having been demonstrated by Fischer, the present work was undertaken to determine if in the case of the simple monocyclic iminazoles, isomerides, such as  $\mathrm{CH}{<}\begin{array}{l}\mathrm{NH\cdot CX}\\ \mathrm{N{-\!-}CY}\end{array}$ and  $\mathrm{CH}{<}\begin{array}{l}\mathrm{N{-\!-}CX}\\ \mathrm{NH\cdot CY}\end{array}$, are capable of separate existence, or if only one tautomeric substance is obtainable. It was shown previously (Abstr., 1893, i, 734) that iminazoles are formed by the action of thiocyanic acid on α-amino-ketones and oxidation of the resulting mercaptans:

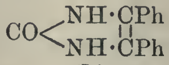


$$\mathrm{COX\cdot CHY\cdot NH_2} \longrightarrow \mathrm{SH\cdot C}{<}\begin{array}{l}\mathrm{NH\cdot CX}\\ \mathrm{N{-\!-}CY}\end{array} \text{ or }$$

$$\mathrm{SH\cdot C}{<}\begin{array}{l}\mathrm{N{-\!-}CX}\\ \mathrm{NH\cdot CY}\end{array} \longrightarrow \mathrm{CH}{<}\begin{array}{l}\mathrm{NH\cdot CX}\\ \mathrm{N{-\!-}CY}\end{array} \text{ or } \mathrm{CH}{<}\begin{array}{l}\mathrm{N{-\!-}CX}\\ \mathrm{NH\cdot CY}\end{array}.$$

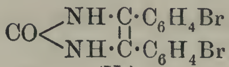
It is argued from the consideration of this scheme that, if the iminazoles be not tautomeric, the iminazole prepared in this manner from α-aminopropiophenone, $\mathrm{COPh\cdot CHMe\cdot NH_2}$, must be isomeric with that derived from α-amino-α-phenylacetone, $\mathrm{COMe\cdot CHPh\cdot NH_2}$. It is found, however, that the two amino-ketones yield the same 4-phenyl-5-methyl- or 5-phenyl-4-methyl-iminazolyl mercaptan (Behr-Bregowski, Abstr., 1897, i, 458), which forms white leaflets, becoming rose-red at about 260°, sinter about 280°, m. p. 298—299°. Phenylmethyliminazole, formed by the oxidation of the mercaptan with nitric acid, crystallises in white leaflets, m. p. 185°, forming a brownish-violet liquid. G. Y.

Bromination of Diphenylglyoxalone. I. Heinrich Biltz and Chaim Rimpel (*Ber.*, 1908, 41, 1754—1760).—When boiled with bromine in chloroform solution and treated with water, diphenylglyoxalone (I) yields 4:5-di-*p*-bromodiphenylglyoxalone (II) together with small amounts of di-*p*-bromobenzil and di-*p*-bromodiphenylacetylenediureine. The main reaction is found to take place in several stages, the first, which is complete at the ordinary temperature, leading to the formation of 4:5-di-*p*-bromodiphenylglyoxalone dibromide (III). At higher temperatures, this is converted by the hydrogen bromide liberated during the first stage into 4-bromo-2-keto-4:5-di-*p*-bromodiphenyltetrahydroglyoxaline (IV), which when treated with water loses hydrogen bromide and forms 4 : 5-di-*p*-bromdiphenylglyoxalone :



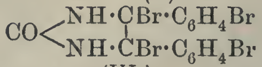
$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CPh}\\ \|\\ \mathrm{NH\cdot CPh}\end{matrix}$$

(I.)



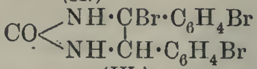
$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C\cdot C_6H_4Br}\\ \|\\ \mathrm{NH\cdot C\cdot C_6H_4Br}\end{matrix}$$

(II.)



$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CBr\cdot C_6H_4Br}\\ |\\ \mathrm{NH\cdot CBr\cdot C_6H_4Br}\end{matrix}$$

(III.)



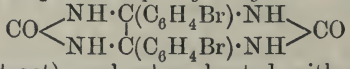
$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CBr\cdot C_6H_4Br}\\ |\\ \mathrm{NH\cdot CH\cdot C_6H_4Br}\end{matrix}$$

(IV.)

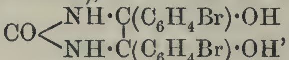
The intermediate substances (III) and (IV) are formed also by the action of bromine and hydrogen bromide respectively on di-*p*-bromodiphenylglyoxalone.

Di-p-*bromodiphenylglyoxalone*, $C_{15}H_{10}ON_2Br_2$, crystallises from alcohol in colourless, rectangular plates, m. p. 328°, or from glacial acetic acid in microscopic needles containing $C_2H_4O_2$, is soluble in alcoholic alkalis, and is oxidised by liquid nitrogen dioxide or concentrated nitric acid, forming *di*-p-*bromobenzil*, $C_6H_4Br\cdot CO\cdot CO\cdot C_6H_4Br$ (see following abstract). In the same manner, diphenylglyoxalone yields benzil when treated with nitric acid or sodium nitrite in concentrated sulphuric acid solution. The *diacetyl* derivative, $C_{15}H_8ON_2Br_2Ac_2$, crystallises in rhombic plates, m. p. 192—193°, and is readily hydrolysed by alcoholic potassium hydroxide.

Di-p-*bromodiphenylglyoxalone dibromide*, $C_{15}H_{10}ON_2Br_4$, prepared by the action of bromine on diphenylglyoxalone or di-*p*-bromodiphenylglyoxalone in glacial acetic acid, chloroform, or benzene solution, crystallises in yellow, rectangular plates and needles, reacts with carbamide, forming *di*-p-*bromodiphenylacetylenediureine*,



$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C(C_6H_4Br)\cdot NH}\\ |\\ \mathrm{NH\cdot C(C_6H_4Br)\cdot NH}\end{matrix}>\mathrm{CO}$$

(see following abstract), and when heated with water is converted into the *glycol*,  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C(C_6H_4Br)\cdot OH}\\ |\\ \mathrm{NH\cdot C(C_6H_4Br)\cdot OH}\end{matrix}$, which decomposes into di-*p*-bromobenzil and carbamide, the latter reacting with unchanged dibromide to form di-*p*-bromodiphenylacetylenediureine. A similar decomposition takes place when the dibromide is treated with sodium hydroxide, but is accompanied by another reaction, leading to the formation of s-*di*-p-*bromodibenzoylcarbamide*,

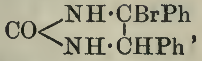
$$C_6H_4Br\cdot CO\cdot NH\cdot CO\cdot NH\cdot CO\cdot C_6H_4Br.$$

When recrystallised from glacial acetic acid, di-*p*-bromodiphenylglyoxalone dibromide decomposes to the extent of about 33%, forming di-*p*-bromodiphenylglyoxalone, di-*p* bromobenzil, and di-*p*-bromodiphenylacetylenediureine. In analogy to this, the same three end products are obtained, in varying proportions, when phenylglyoxalone is treated with bromine in concentrated sulphuric acid and the resulting dibromide precipitated by addition of ice, or when diphenylglyoxalone is allowed to remain in contact with bromine and water.

4-*Bromo*-2-*keto*-4 : 5-*di*-p-*bromodiphenyltetrahydroglyoxaline*,

$$C_{15}H_{11}ON_2Br_3,$$

prepared by the action of bromine and hydrogen bromide on di-*p*-bromodiphenylglyoxalone in chloroform solution, crystallises in light brown prisms, decomp. about 240°, and loses hydrogen bromide, forming di-*p*-bromodiphenylglyoxalone when boiled with xylene, or more slowly when boiled with alcohol, glacial acetic acid, or ether.

4-*Bromo*-2-*keto*-4 : 5-*diphenyltetrahydroglyoxaline*, 
$\mathrm{CO}<\begin{array}{l}\mathrm{NH\cdot CBrPh}\\ \mathrm{NH\cdot CHPh}\end{array}$, prepared by saturating a chloroform solution of diphenylglyoxalone with hydrogen bromide, crystallises in colourless prisms, and loses hydrogen bromide when treated with water.

s-Di-*p*-bromodibenzoylcarbamide, obtained on adding chromic anhydride to 4 : 5-di-*p*-bromodiphenylglyoxalone in boiling glacial acetic acid solution, or by oxidising the dibromo-compound with sodium hypobromite, crystallises in needles, m. p. 250° (decomp.) when quickly, or 245—247° (decomp.) when slowly, heated, forming *p*-bromobenzonitrile, is readily soluble in nitrobenzene, and on hydrolysis with alcoholic alkalis yields *p*-bromobenzoic acid.

When reduced with sodium and alcohol, di-*p*-bromodiphenylglyoxalone yields *diphenyldihydroglyoxalone*, m. p. 292—293°.

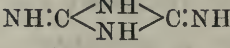
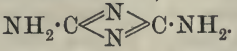
G. Y.

Bromination of Diphenylglyoxalone. II. Heinrich Biltz (*Ber.*, 1908, 41, 1761—1767. Compare preceding abstract).—The action of bromine on diphenylglyoxalone in boiling glacial acetic acid solution leads to the formation of di-*p*-bromobenzil, di-*p*-bromodiphenylacetylenediureine, and 5 : 5-di-*p*-bromodiphenylhydantoin (this vol., i, 462).

Di-*p*-bromobenzil, $C_{14}H_8O_2Br_2$, crystallises from benzene in flat needles, m. p. 228—229°, gives colour reactions with boiling alcoholic and aqueous alcoholic alkalis, and with alcoholic potassium hydroxide at the ordinary temperature forms a yellow solution which on acidification yields a slowly solidifying *oil*. Oxidation of di-*p*-bromobenzil with chromic anhydride in glacial acetic acid solution leads to the formation of *p*-bromobenzoic acid.

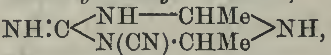
Di-*p*-bromodiphenylacetylenediureine, $C_{16}H_{12}O_2N_4Br_2$, is formed by heating di-*p*-bromobenzil with carbamide, or by the action of bromine and carbamide on di-*p*-bromophenylglyoxalone, diphenylglyoxalone, or benzoin, in glacial acetic acid solution at the ordinary temperature. It crystallises in colourless threads or leaflets, decomp. about 360°, does not form an acetyl derivative (compare Biltz, this vol., i, 62), is stable towards concentrated sulphuric acid, sodium nitrite in concentrated sulphuric or glacial acetic acid solution, and bromine, and is only slightly attacked by aqueous or alcoholic potassium hydroxide, but is decomposed by fuming nitric acid.

Di-*p*-bromodiphenylglyoxalone forms small amounts of di-*p*-bromobenzil when heated with concentrated hydrochloric acid at 160—170°, but remains unchanged when boiled with hydrogen bromide in glacial acetic acid solution; when boiled with bromine, acetic acid, and water, on the other hand, it is rapidly decomposed, forming di-*p*-bromobenzil together with small amounts of di-*p*-bromodiphenylacetylenediureine and di-*p*-bromodiphenylhydantoin. G. Y.

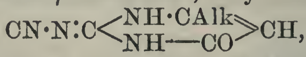
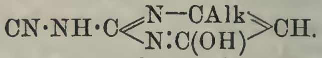
Dicyanodiamide. Franz Pohl (*J. pr. Chem.*, 1908, [ii], 77, 533—548).—Although the object of numerous investigations, the constitution of dicyanodiamide has not hitherto been established with certainty. Baumann (this Journ., 1873, 1025; 1874, 376) ascribed to dicyanodiamide the formula  $NH{:}C{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C{:}NH$, whilst Klason (Abstr., 1886, 324) and Hofmann (Abstr., 1886, 41) preferred the form  $NH_2{\cdot}C{<}\genfrac{}{}{0pt}{}{N}{N}{>}C{\cdot}NH_2$. Bamberger, on the other hand, considered the substance to be a cyanoguanidine, $NH{:}C(NH_2){\cdot}NH{\cdot}CN$ (Abstr., 1883, 907, 1090); in discussing this constitution, it is necessary to take into consideration the tautomeric form $CN{\cdot}N{:}C(NH_2)_2$. The present author has found that, on treatment with sodium hypobromite solution, dicyanodiamide readily loses half its nitrogen, a behaviour which points to the presence of two amino-groups. When heated with 2 mols. of benzoic anhydride, dicyanodiamide forms benzoic acid, benzonitrile, carbon dioxide, dibenzoylcarbamide, and *dibenzoyldicyanodiamide*, $CN{\cdot}N{:}C(NHBz)_2$. With formaldehyde, dicyanodiamide forms an additive compound, *cyanohydroxymethylguanidine*,

$$OH{\cdot}CH_2{\cdot}NH{\cdot}C(NH_2){:}N{\cdot}CN,$$

but with acetaldehyde and ammonia a compound, which is probably 1-*imino*-6-*cyano*-3 : 5-*dimethylhexahydrotriazine*,



$$NH{:}C{<}\genfrac{}{}{0pt}{}{NH\text{——}CHMe}{N(CN){\cdot}CHMe}{>}NH,$$

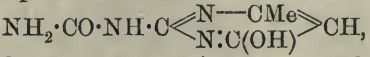
is formed, whilst with the sodio-β-keto-esters, dicyanodiamide forms 2-cyanoimino-4-alkyluracils,  $CN{\cdot}N{:}C{<}\genfrac{}{}{0pt}{}{NH{\cdot}CAlk}{NH\text{—}CO}{>}CH$, or 2-cyanoamino-6-keto-4-alkylpyrimidines,  $CN{\cdot}NH{\cdot}C{<}\genfrac{}{}{0pt}{}{N\text{—}CAlk}{N{:}C(OH)}{>}CH$. It is considered that these reactions show that dicyanodiamide reacts in both of the tautomeric forms of cyanoguanidine.

Dibenzoyldicyanodiamide, $C_{16}H_{12}O_2N_4$, crystallises in needles, m. p. 225° (compare Gerlich, this Journ., 1876, ii, 196), is readily soluble in cold dilute alkalis, and when heated with hydrochloric acid under pressure yields benzoic acid.

If dicyanodiamide and benzoic anhydride are heated together in molecular proportions, the product contains benzonitrile, benzoic acid, and a *substance*, $C_9H_8ON_2$, white needles, m. p. 162—163°, but not dibenzoyldicyanodiamide.

Cyanohydroxymethylguanidine, $C_3H_6ON_4$, is obtained as a white, crystalline powder, m. p. 118°, yields formaldehyde and dicyanodiamide when heated with water, and forms unstable *compounds* with silver and mercuric salts and with platinum tetrachloride in hydrochloric acid solution.

1-Imino-6-cyano-3 : 5-dimethylhexahydrotriazine, $C_6H_{11}N_5$, crystallises in white needles, m. p. 190°, and is readily decomposed, forming ammonia, acetaldehyde, and dicyanodiamide when boiled with water, or more rapidly with dilute alkalis, or when heated with dilute hydrochloric acid at 40° for thirty minutes. The *picrate*, $C_{12}H_{16}O_8N_8$, was analysed. The *nitroso*-derivative, $C_6H_{10}ON_6$, forms yellow needles, m. p. 156°. The triazine reacts with aniline hydrochloride, forming ethylideneaniline, or with phenylhydrazine hydrochloride, forming phenylethylidenehydrazine.

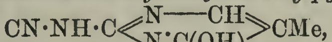
2-*Cyanoamino*-6-*hydroxy*-4-*methylpyrimidine*, $C_6H_6ON_4$, prepared from dicyanodiamide and ethyl acetoacetate, separates from acetic acid in crystals, which become yellow at 240°, decomp. 280—285°. The *sodium* salt, $C_6H_5ON_4Na,H_2O$, loses H_2O at 180—190°, decomp. 290°, and in aqueous solution gives characteristic precipitates with metallic salts. The *silver* salt, $C_6H_5ON_4Ag$, was analysed. When boiled with hydrochloric acid, the cyanoamino-compound is converted into 2-*carbamido*-6-*hydroxy*-4-*methylpyrimidine*,  $NH_2\cdot CO\cdot NH\cdot C<\begin{matrix}N{-}{-}CMe\\N{:}C(OH)\end{matrix}>CH$, which is obtained as a white, flocculent substance, sinters at 229°, m. p. 262—264° becoming yellow. When heated with concentrated hydrochloric acid at 120°, the cyanoamino-compound is converted into iminomethyluracil.

2-*Cyanoamino*-6-*hydroxy*-4-*phenylpyrimidine*, $C_{11}H_8ON_4$, prepared from dicyanodiamide and ethyl benzoylacetate, crystallises in needles, which sinter at 230°, but do not melt. 2-*Carbamido*-6-*hydroxy*-4-*phenylpyrimidine*, $C_{11}H_{10}O_2N_4$, is a white, amorphous powder, m. p. 234°.

2-*Cyanoamino*-6-*hydroxy*-4 : 5-*dimethylpyrimidine*, $C_7H_8ON_4$, prepared from dicyanodiamide and ethyl methylacetoacetate, crystallises from boiling alcohol in leaflets, m. p. 280° (decomp.), yields iminodimethyluracil when heated with concentrated hydrochloric acid, and when boiled with dilute hydrochloric acid is converted into 2-*carbamido*-6-*hydroxy*-4 : 5-*dimethylpyrimidine*, m. p. 269° (decomp.).

2-*Cyanoamino*-6-*hydroxy*-4-*methyl*-5-*ethylpyrimidine*, prepared from ethyl ethylacetoacetate, is obtained as a crystalline powder, m. p. 257° (decomp.); the corresponding 2-*carbamido*-compound forms needles, m. p. 235°.

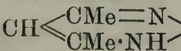
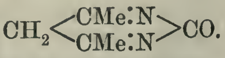
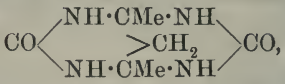
The action of dicyanodiamide on ethyl sodioformylpropionate leads to the formation of 2-*cyanoamino*-6-*hydroxy*-5-*methylpyrimidine*,

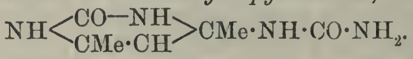


$$CN\cdot NH\cdot C<\begin{matrix}N{-}{-}CH\\N{:}C(OH)\end{matrix}>CMe,$$

which crystallises from hot water in needles, becomes yellow, but does not melt, at 293°, when heated with fuming hydrochloric acid at 120° is hydrolysed to carbon dioxide, ammonia, formic acid, and propionic acid, and when boiled with dilute hydrochloric acid yields 2-*carbamido*-6-*hydroxy*-5-*methylpyrimidine*, crystallising in needles, m. p. 245°.

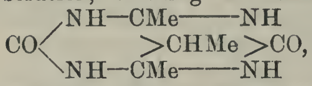
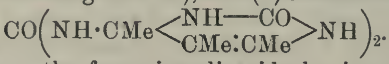
G. Y.

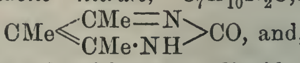
Condensation of β-Diketones with Carbamide. T. DE HAAN (*Rec. trav. chim.*, 1908, 27, 162—191. Compare Evans, Abstr., 1893, i, 129; 1894, i, 111).—The compound obtained by Evans on condensing carbamide with acetylacetone crystallises with $2H_2O$ in monoclinic prisms. These are colourless when freshly prepared, but by warming in aqueous solution or on exposure to light are transformed without change of crystalline form into a yellow modification. The colourless compound is probably 4 : 6-dimethyl-2-pyrimidone,  $CH<\begin{matrix}CMe{=}N\\CMe\cdot NH\end{matrix}>CO$, whilst the yellow modification may possess the constitution originally ascribed to it by Evans,  $CH_2<\begin{matrix}CMe{:}N\\CMe{:}N\end{matrix}>CO$. The *potassium* salt is colourless, and when treated with carbon dioxide yields the colourless substance. The *nitrate* decomposes explosively at 245°. When acetylacetone is mixed with excess of carbamide in aqueous solution, *βδ-pentanediureide*,  $\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH\cdot CMe\cdot NH}\\ \qquad >\mathrm{CH_2}\\ \mathrm{NH\cdot CMe\cdot NH}\end{array}\right\rangle\mathrm{CO}$, is formed together with the diuriminoacetylacetone described by Combes (compare Abstr., 1893, i, 454). The former compound crystallises from water in lustrous plates containing $4H_2O$. The anhydrous substance has m. p. 290°. Cold nitric acid converts it into a *dinitrate*, but, on warming, this is decomposed into carbamide and 2-oxy-4 : 6-dimethylpyrimidine. The colourless modification of Combes' compound is probably 6-*carbamido*-4 : 6-*dimethyl-2-pyrimidone*,



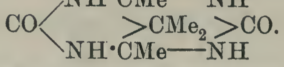
$$\mathrm{NH}\left\langle\begin{array}{l}\mathrm{CO-NH}\\ \mathrm{CMe\cdot CH}\end{array}\right\rangle\mathrm{CMe\cdot NH\cdot CO\cdot NH_2}.$$

A yellow form can also be obtained, and this is regarded as a derivative of the coloured variety of 4 : 6-dimethyl-2-pyrimidone.

Methylacetylacetone and carbamide readily condense in aqueous solution, forming a mixture of (1) *γ-methyl-βδ-pentanediureide*,  $\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH-CMe-NH}\\ \qquad >\mathrm{CHMe}\\ \mathrm{NH-CMe-NH}\end{array}\right\rangle\mathrm{CO}$, which separates from water as brilliant white, monoclinic crystals containing $2H_2O$ (the anhydrous substance darkens without melting at 316°), and (2) *carbamidobis-4:5:6-trimethyl-2-pyrimidone*,  $\mathrm{CO}\left(\mathrm{NH\cdot CMe}\left\langle\begin{array}{l}\mathrm{NH-CO}\\ \mathrm{CMe{:}CMe}\end{array}\right\rangle\mathrm{NH}\right)_2$. This compound, distinguished from the foregoing diureide by its solubility in alcohol, forms white needles, m. p. 209—210° with effervescence. It separates with $2H_2O$ from aqueous solution.

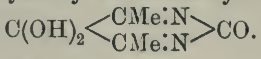
A solution of either of the two preceding compounds in nitric acid evolves carbon dioxide and nitrous oxide, and deposits the yellow unstable 4 : 5 : 6-*trimethyl-2-pyrimidone nitrate*, $C_7H_{10}N_2O,HNO_3$. The free base has the constitution  $\mathrm{CMe}\left\langle\!\!\left\langle\begin{array}{l}\mathrm{CMe{=}N}\\ \mathrm{CMe\cdot NH}\end{array}\right\rangle\right.\mathrm{CO}$, and, when obtained by decomposing its *potassium* salt with carbon dioxide, forms colourless needles, which separate from water with $1\frac{1}{2}H_2O$.

Dimethylacetylacetone and carbamide condense when heated together at 140—160°, forming *γγ-dimethyl-βδ-pentanediureide*,



$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH\cdot CMe-NH}\\ \qquad >\mathrm{CMe_2}\\ \mathrm{NH\cdot CMe-NH}\end{array}\right\rangle\mathrm{CO}.$$

This separates from water in colourless crystals, m. p. 270°, which contain $2H_2O$. Nitric acid converts it into a substance, m. p. 266°. This is probably 5 : 5-dihydroxy-4 : 6-dimethyl-2-pyrimidone,

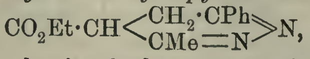


$$\mathrm{C(OH)_2}\left\langle\begin{array}{l}\mathrm{CMe{:}N}\\ \mathrm{CMe{:}N}\end{array}\right\rangle\mathrm{CO}.$$

W. O. W.

Action of Hydrazine on Ethyl Phenacylacetoacetate. CARL BÜLOW AND HANS FILCHNER (*Ber.*, 1908, 41, 1886—1889).—Paal and Kühn (this vol., i, 57) have studied the action of hydrazine on ethyl phenacylbenzoylacetate, and the present authors now describe experiments with ethyl phenacylacetoacetate, which gives rise to a similar condensation product.

Ethyl 6-*phenyl*-3-*methyl*-4 : 5-*dihydropyridazine*-4-*carboxylate*,

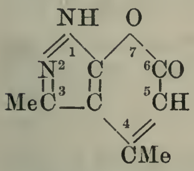


$$CO_2Et\cdot CH<\begin{matrix}CH_2\cdot CPh\\ CMe=N\end{matrix}>N,$$

obtained by adding hydrazine hydrate to ethyl phenacylacetoacetate below 0°, crystallises from light petroleum in aggregates of yellow needles, m. p. 90—91°. It is not attacked by nitrous acid.

J. C. C.

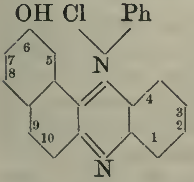
3 : 4-Dimethyl-1 : 2-pyrazo-6 : 7-pyrone (Lactone of 5-Hydroxy-3-methylpyrazole-4-*iso*propylenecarboxylic Acid). CARL BÜLOW and FRITZ SCHAUB (*Ber.*, 1908, **41**, 1945—1947).—The substance $C_8H_8O_2N_2$, m. p. 246—247°, which has been obtained in various ways (Knorr and Rosengarten, Abstr., 1894, i, 546; Wolff, Abstr., 1905, i, 839; Bülow and Lobeck, Abstr., 1907, i, 301), has been shown to have the annexed constitution by Stollé (Abstr., 1905, i, 838) and Wolff (*loc. cit.* this vol., i, 291).



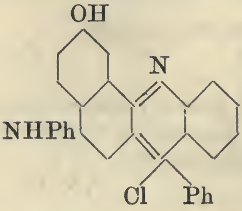
The formation of the lactone from ethyl oxalylbishydrazoneacetoacetate at 187° (Bülow and Lobeck, *loc. cit.*), and from ethyl acetoacetatebenzoylhydrazone at 175°, leads the authors to the general statement that the action of heat under suitable conditions on ethyl acetoacetate-acylhydrazones results in the formation of a diacylhydrazine and 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone.

C. S.

Azonium Compounds and Azines from 7-Hydroxy-β-naphthaquinone. FRIEDRICH KEHRMANN and R. BRUNEL (*Ber.*, 1908, **41**, 1832—1837).—Azonium compounds containing a hydroxyl group in the meta- or para-position to the ammonium group are often converted into inner salts of a phenol-betaine character when the free bases are liberated from their salts. Thus the meta-series give *apo*safranones, rosindones, and *iso*rosindones, and the para-series the prasindones. The authors have now examined the behaviour of similar compounds containing a hydroxyl group in a different position, and find that in the case of 6-hydroxyphenyl*iso*naphthaphenazonium chloride, annexed formula, the free base is a true ammonium base and does not form inner salts. 6-*Hydroxyphenyl*iso*naphthaphenazonium chloride,* formed by condensing *o*-phenylenephenyldiamine and 7-hydroxy-β-naphthaquinone, is obtained in black, shining leaflets. The *platinichloride* is brownish-violet. The *base* is formed by shaking the hydrochloride with silver hydroxide, but could not be isolated from the green solution. The *acetyl* derivative of the chloride is orange-red, and gives a *nitrate*, $C_{24}H_{17}O_2N_2\cdot NO_3,H_2O$, brownish-red needles, a *platinichloride*, scarlet, crystalline powder, and a *dichromate*, long needles. By treating 6-hydroxyphenyl*iso*naphthaphenazonium chloride with aniline, 3-*anilino*-6-*hydroxyphenyl*iso*naphthaphenazonium*



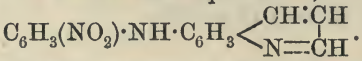
chloride, dark blue crystals with a coppery lustre, is obtained. The fact of this substance having a blue colour was crucial in deciding on the constitution of the parent substance, for from analogy the anilino-derivative of the isomeric 9-hydroxynaphthaphenazonium chloride, annexed formula, should be red. A small amount of this substance was contained in the mother liquor from the condensation, and was found to give a violet-red derivative with aniline.



9-*Hydroxynaphthaphenazonium chloride*, steel-blue crystals, gives a *platinichloride*. The free *base* is bluish-green, and could only be obtained in solution.

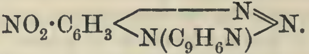
9-*Hydroxynaphthaphenazine*, $HO\cdot C_{10}H_5{\ll}\begin{smallmatrix}N\\N\end{smallmatrix}{\gg}C_6H_4$, obtained from *o*-phenylenediamine hydrochloride and 7-hydroxy-β-naphthaquinone, crystallises from alcohol in yellow leaflets, m. p. 285°; the *hydrochloride* forms golden crystals. J. C. C.

Condensation Products of Chlorodinitrobenzene and Aminoquinolines. Wilhelm Meigen, H. Garbs, W. Merkelbach, and G. Wichern (*J. pr. Chem.*, 1908, [ii], **77**, 472—488).—1-Chloro-2 : 4-dinitrobenzene reacts with 6- and 7-aminoquinolines in boiling alcoholic solution, or with 5- and 8-aminoquinolines when fused, forming the corresponding 2 : 4-dinitroanilinoquinolines,



$$C_6H_3(NO_2)\cdot NH\cdot C_6H_3{<}\begin{array}{l}CH{:}CH\\ N{=}CH\end{array}.$$

These, on reduction with ammonium sulphide, yield 4-nitro-2-aminoanilinoquinolines, $NH_2\cdot C_6H_3(NO_2)\cdot NH\cdot C_9H_6N$, which are converted by nitrous acid into 5-nitro-1-quinolylbenzotriazoles,



$$NO_2\cdot C_6H_3{<}\begin{array}{l}\text{——}N\\ N(C_9H_6N)\end{array}{\gg}N.$$

Reduction of the dinitro-compounds with stannous chloride and hydrochloric acid leads to the formation of 2 : 4-diaminoanilinoquinolines, $C_6H_3(NH_2)_2\cdot NH\cdot C_9H_6N$.

8-op-*Dinitroanilinoquinoline* crystallises in orange needles, m. p. 266°; the *platinichloride*, $(C_{15}H_{10}O_4N_4)_2,H_2PtCl_6$, brownish-yellow needles, m. p. 280°. 8-p-*Nitro*-o-*aminoanilinoquinoline*, brown needles, m. p. 231°; the *hydrochloride*, $C_{15}H_{12}O_2N_4,HCl$, needles; the *platinichloride*, $(C_{15}H_{12}O_2N_4)_2,H_2PtCl_6$, brownish-yellow crystals, m. p. 276°; the *acetyl* derivative, $C_{17}H_{14}O_3N_4$, yellow needles, m. p. 172°. 5-*Nitro*-1-o-*quinolylbenzotriazole*, yellow needles, m. p. 274°, forms unstable salts. 8-op-*Diaminoanilinoquinoline*, $C_{15}H_{14}N_4,H_2O$, yellowish-green needles, m. p. 129°,

7-op-*Dinitroanilinoquinoline* forms brownish-yellow crystals, m. p. 204°. 7-p-*Nitro*-o-*aminoanilinoquinoline*, dark red needles, m. p. 215°. 5-*Nitro*-1-m-*quinolylbenzotriazole*, m. p. 290°.

6-op-*Dinitroanilinoquinoline* crystallises in red needles, m. p. 217°; the *platinichloride* forms yellow leaflets. 6-p-*Nitro*-o-*aminoanilinoquinoline* is obtained as a red powder, m. p. 215°. 5-*Nitro*-1-

p-*quinolylbenzotriazole*, white needles, m. p. 274°. 6-op-*Diaminoanilinoquinoline*, silver-grey needles, m. p. 173°, forms yellow salts.

5-op-*Dinitroanilinoquinoline* crystallises from xylene in yellowish-red needles, m. p. 211°, and forms salts which are decomposed by water; the *hydrochloride* and *platinichloride* were analysed. The *methiodide*, $C_{15}H_{10}O_4N_4$,MeI, formed by heating the dinitro-base with methyl iodide at 100°, crystallises in yellow needles, m. p. 164°, and yields a dark violet *precipitate* when treated with an alkali. 5-p-*Nitro*-o-*aminoanilinoquinoline*, brown needles, m. p. 232°; the *platinichloride*, brown leaflets, m. p. 276°. The *acetyl* derivative, yellow crystals, m. p. 215°. 5-*Nitro*-1-ana-*quinolylbenzotriazole*, needles, m. p. 227°. 5-op-*Diaminoanilinoquinoline*,

$$C_{15}H_{14}N_4,H_2O,$$

yellowish-green needles, m. p. 191°. G. Y.

Action of *as*-**Phenylbenzylhydrazine on Carbamide.** HUGO MILRATH (*Ber.*, 1908, **41**, 1865—1869).—Phenylbenzylsemicarbazide, obtained by heating carbamide with *as*-phenylbenzylhydrazine at 175°, or by warming equivalent quantities of the hydrazine hydrochloride and potassium cyanate in aqueous solution, has m. p. 139—140°; Michaelis (this vol., i, 471) gives m. p. 103°. The *diacetyl* derivative, $C_{17}H_{18}O_2N_2$, crystallises in glistening needles, m. p. 128°.

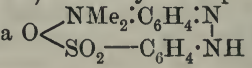
Diphenyldibenzylcarbazide, $(CH_2Ph\cdot NPh\cdot NH)_2CO$, m. p. 169°, is formed when *as*-phenylbenzylhydrazine (2 mol.) is heated with carbamide (1 mol.) at 175° or with phenylbenzylsemicarbazide at a temperature not above 180°. On the contrary, a *substance*, $C_{14}H_{12}ON_2$, m. p. 167—168°, is obtained when *as*-phenylbenzylhydrazine and carbamide are heated together at 270°; the *acetate* has m. p. 81—82°; the *benzoate* crystallises in broad, glassy needles, m. p. 82°; a crystalline *methyl* derivative was also prepared.

It is probable that the compound described by Michaelis (*loc. cit.*) as diphenylbenzylaminobiuret is identical with the substance, m. p. 167—168°. W. H. G.

Action of Dilute Nitric Acid on Helianthin. JOHN J. FOX (*Ber.*, 1908, **41**, 1989—1991).—When methyl-orange is mixed with dilute nitric acid at the ordinary temperature, the dye is decomposed with formation of 2:4-dinitromethylaniline, a methyl group being eliminated. If the mixture is kept cold, the presence of a diazo-compound can also be detected. The author considers that a mononitrohelianthin may be first formed, which then assumes the quinonoid structure and simultaneously loses a methyl group, thus:

$$HSO_3\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(NO_2)\cdot NMe_2 \longrightarrow$$
$$HSO_3\cdot C_6H_4\cdot NH\cdot N{:}C_6H_3(NO_2){:}NMe + CH_3\cdot NO_3.$$

The product is then decomposed with formation of dinitromethylaniline and diazobenzenesulphonic acid. J. C. C.

Aminoazo-compounds. JOHN T. HEWITT (*Ber.*, 1908, **41**, 1986—1988).—A claim for priority. The theory of the constitution of the two forms of aminoazobenzenesulphonic acids recently put forward by Hantzsch (this vol., i, 469) had already been advanced by the author (this vol., ii, 269). The decomposition of helianthin by dilute nitric acid (Fox, preceding abstract) can only be explained on the assumption of the quinonoid formula  $O<\begin{matrix}NMe_2:C_6H_4:N \\ SO_2—C_6H_4\cdot NH\end{matrix}$ for the free acid.

Benzeneazo-2 : 6-dibromoaniline has m. p. 168° (corr.), and not 191° (Hantzsch and Hilscher, this vol., i, 485). J. C. C.

Action of Diazo-salts on Primary Dinitrohydrocarbons. GIACOMO PONZIO and G. CHARRIER (*Gazzetta*, 1908, **38**, i, 526—532).—The reaction previously described (this vol., i, 482) for ω-dinitrotoluene is extended to ω-dinitro-*p*-xylene and -*p*-methoxytoluene. In these cases, too, the diazobenzene derivatives, $CR(N_2O_4):N_2Ph$, readily undergo transformation into the isomeric α-nitro-β-nitroso-α-acyl-β-phenylhydrazines, $R\cdot CO\cdot N(NO_2)\cdot NPh\cdot NO$, and benzeneazodinitrohydrocarbons, $N_2Ph\cdot CR(NO_2)_2$.

The *diazobenzene* derivative of *ω-dinitro*-p-*xylene*,

$$C_6H_4Me\cdot C(N_2O_4):N_2Ph,$$

m. p. 72° (decomp.), has a golden-yellow colour, dissolves in concentrated sulphuric acid, giving a green coloration, changes slowly into the isomeric red azo-compound, and gives off nitrogen when heated with alcohol.

α-Nitro-β-nitroso-α-p-*toluoyl-β-phenylhydrazine*,

$$C_6H_4Me\cdot CO\cdot N(NO_2)\cdot NPh\cdot NO,$$

prepared by dissolving the diazobenzene derivative of ω-dinitro-*p*-xylene in anhydrous benzene, separates from the latter in unstable, white laminæ, m. p. 97—98° (decomp.), gives a brown coloration with concentrated sulphuric acid and phenol, and dissolves in cold water, giving a solution which almost immediately deposits *β-nitroso-α*-p-*toluoyl-β-phenylhydrazine*, $C_6H_4Me\cdot CO\cdot NH\cdot NPh\cdot NO$, in the form of faintly yellow laminæ, m. p. 115—116° (decomp.).

ω-Dinitro-ω-benzeneazo-p-*xylene*, $NPh:N\cdot C(NO_2)_2\cdot C_6H_4Me$, prepared from the diazobenzene derivative of ω-dinitro-*p*-xylene by heating it with alcohol or dissolving it in aqueous ether, crystallises from alcohol in orange-red prisms, m. p. 130—135° (decomp.).

The *diazobenzene* derivative of *ω-dinitro*-p-*methoxytoluene*,

$$OMe\cdot C_6H_4\cdot C(N_2O_4):N_2Ph,$$

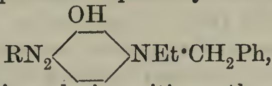
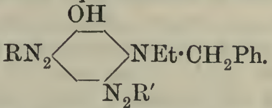
is an unstable, yellow compound, m. p. 85° (decomp.), and dissolves in concentrated sulphuric acid, giving an emerald-green solution.

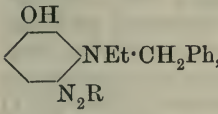
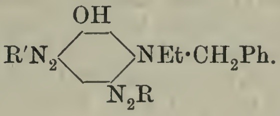
α-Nitro-β-nitroso-α-anisoyl-β-phenylhydrazine,

$$OMe\cdot C_6H_4\cdot CO\cdot N(NO_2)\cdot NPh\cdot NO,$$

separates rapidly from an ice-cold anhydrous benzene solution of the diazobenzene derivative of ω-dinitro-*p*-methoxytoluene in unstable, yellow laminæ, m. p. 123—124° (decomp.), and gives an emerald-green coloration with concentrated sulphuric acid and phenol; it dissolves in cold water, which rapidly transforms it into nitric acid and β-nitroso-α-anisoyl-β-phenylhydrazine (compare Bamberger and Pemsel, Abstr., 1903, i, 286). Boiling water converts the latter into α-anisoyl-β-phenylhydrazine, with evolution of nitrous vapours and partial resinification.

ω-Dinitro-ω-benzeneazo-p-*methoxytoluene*, $NPh{:}N{\cdot}C(NO_2)_2{\cdot}C_6H_4{\cdot}OMe$, is formed spontaneously from the diazobenzene derivative of ω-dinitro-*p*-methoxytoluene, or, more rapidly, in alcoholic, ethereal, or chloroform solution, or by shaking the benzene solution with water. It separates in blood-red, flattened needles, m. p. 141—148° (decomp.), and is moderately stable. T. H. P.

Primary Bisazo-compounds of Benzylethyl-*m*-aminophenol. Carl Bülow and Theodor Sproesser (*Ber.*, 1908, 41, 1684—1692. Compare Bülow and Wolfs, Abstr., 1898, i, 308; 1899, i, 135; Bülow and Sproesser, this vol., i, 272).—The authors find that two isomeric bisazo-compounds can be obtained at will from benzylethyl-*m*-aminophenol under suitable conditions. If the substituted *m*-aminophenol in an aqueous solution slightly acidified with hydrochloric acid is treated with an equivalent quantity of a diazo-salt, $RN_2{\cdot}X$, the monoazo-compound, , is obtained, which reacts in an alcoholic alkaline solution with another equivalent of a diazo-salt, $R'N_2{\cdot}X$, to yield the bisazo-compound .

Conversely, benzylethyl-*m*-aminophenol can be coupled in alkaline solution with an equivalent quantity of $RN_2{\cdot}X$, yielding , which can then unite with $R'N_2{\cdot}X$ in acetic acid solution, forming . The following compounds are described.

5-*Benzylethylamino-2-benzeneazophenol*,

$$N_2Ph{\cdot}C_6H_3(OH){\cdot}NEt{\cdot}CH_2Ph,$$

m. p. 117°, red crystals with blue reflex. 5-*Benzylethylamino*-2-p-*tolueneazophenol*, $C_{22}H_{23}ON_3$, m. p. 110°, orange-red crystals. 5-*Benzylethylamino-2-α-naphthaleneazophenol*, $C_{25}H_{23}ON_3$, m. p. 110°, greenish-black crystals. 5-*Benzylethylamino-2-benzeneazophenetole*, $C_{23}H_{25}ON_3$, m. p. 103·5°, orange-red leaflets. 5-*Benzylethylamino*-2-p-*sulphobenzeneazophenol*, $C_{21}H_{21}O_4N_3S$, m. p. 230°, small, red crystals; the *sodium* salt contains $2H_2O$, and has m. p. 258—268° (decomp.).

5-*Benzylethylamino*-2 : 4-*bisbenzeneazophenol*, $C_{27}H_{25}ON_5$, m. p. 129°, greenish-black crystals with a metallic lustre, which dissolve in concentrated sulphuric acid with a green colour, becoming red on dilution. 5-*Benzylethylamino*-2 : 4-*bis*-p-*tolueneazophenol*, $C_{29}H_{29}ON_5$, m. p. 154°, green prisms. 5-*Benzylethylamino-2-benzeneazo*-4-p-*tolueneazophenol*, $C_{28}H_{27}ON_5$, m. p. 116°, highly refractive, green crystals, red by transmitted light. C. S.

Deaminoproteins. Zdenko H. Skraup (*Biochem. Zeitsch.*, 1908, **10**, 245—248. Compare Abstr., 1906, i, 913; 1907, i, 367, 739).—Deaminoproteins, obtained by the action of nitrous acid, generally contain slightly less nitrogen than the proteins from which they are derived. This diminution in the nitrogen content is apparently connected with a considerable reduction of the amount of histidine and arginine, and a complete disappearance of lysine among the products of hydrolysis. G. B.

The So-called Amidic Nitrogen of the Proteins. Zdenko H. Skraup and Emil R. von Hardt-Stremayr (*Monatsh.*, 1908, **29**, 255—262).—In the investigations hitherto recorded on the quantities of ammonia formed on the hydrolysis of proteins with hydrochloric acid, the protein has been boiled for some hours with concentrated hydrochloric acid (compare Hausmann, Abstr., 1899, i, 653; 1900, i, 317; Kutscher, Abstr., 1901, i, 107). The present communication contains the results of several determinations of the quantities of ammonia formed by boiling various proteins with both strong and dilute hydrochloric acid for from five minutes to five hours. The substances examined and the maximum amounts of ammonia they yield when boiled with hydrochloric acid are as follows: casein, 1·6%; edestin, 1·6%; serum-globulin, 1·0%; crystallised egg-albumin, 1·1%; sodium hysalbinate, 0·7%, and sodium protalbinate, 1·0%. Gelatin was also examined, but, contrary to the statement of Hart (Abstr., 1901, i, 783), was found to contain no amidic nitrogen.

The maximum of amidic nitrogen is obtained by boiling with the strong acid for about five hours, but about two-thirds of the total amidic nitrogen is eliminated during the first five minutes when strong hydrochloric acid is used, and in fifteen minutes when dilute acid (1 : 1) is employed. The conclusion is drawn therefore that the greater part of the amidic nitrogen is eliminated during the transformation of the protein into the albumose, and that consequently the formation of the albumose from the protein is not simply a hydrolytic process, but is accompanied by the liberation of ammonia.

Ammonia is also probably evolved during the further dissociation of the albumose (compare Henderson, Abstr., 1900, i, 265).

W. H. G.

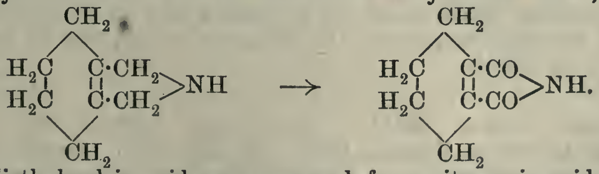
Protoplasmic Hydrolysis. Aléxandre Étard and Antony Vila (*Compt. rend.*, 1908, **146**, 1155—1156).—The author discusses the conditions required for the hydrolysis of protoplasmides and the means of separating the products, pointing out important objections to the use of phosphotungstic acid. The fact is emphasised that in protoplasmic hydrolysis the true weight of the initial organic matter is never known, owing to the impossibility of completely drying it. The conclusions are drawn that the nitrogenous compounds resulting from the breaking down of protoplasmides are produced in very small quantities, that the high yields proceed from calculations of nitrogen based on hypothesis and not on experience, and that precipitates of high molecular weight give an inexact idea of the true amount of organic matter that they contain. E. H.

Action of Certain Oxidising Agents on Blood Pigments. JOHN A. MACWILLIAM (*Bio.-Chem. J.*, 1908, 3, 155—164).—If strong solutions of chlorates are added to blood, there is beyond the phase of methæmoglobin a jellying effect. The jelly is firm, and its formation is accelerated by acidification or by warmth (30—40°), and retarded by alkalis. The red colour in time gives place to a deep green as seen by reflected light, although thin slices appear brownish-red by transmitted light. The green colour gradually changes to yellow. Sometimes the jelly contracts, squeezing out a clear fluid rich in protein, but free from iron. If the blood is diluted beyond a certain point, jellying fails, and a coloured precipitate is formed when a chlorate is added; this rapidly becomes green if acid is added. Bromates produce similar effects, but iodates produce a red precipitate with different properties. Chlorates and bromates produce the same effects with hæmoglobin solutions, but not with stromata, serum, plasma, or egg-albumin. Solutions of hæmatin fail to give the results also. The altered hæmoglobin is very insoluble; it, however, dissolves in alkali, dries to a dark powder, and microscopically polygonal flakes are seen. It shows no absorption bands. The product is probably due to oxidation, and is not a halogen compound.

The substance retains all the iron of the hæmoglobin in very firm combination. It is digestible by peptic or tryptic enzymes, but there is no formation of hæmatin; on prolonged digestion, the iron is gradually liberated. It is suggested that chlorates and bromates may be useful in distinguishing hæmoglobin from other pigments, and as fixing agents for hæmoglobin in microscopical work. W. D. H.

Hæmatin. WILLIAM KÜSTER [with K. FUCHS] (*Zeitsch. physiol. Chem.*, 1908, 55, 505—556. Compare this vol., i, 303).—Further experiments were carried out on the reduction of the synthesised anhydrides of the methylethylmaleic and methylpropylmaleic acids to the corresponding succinic acids. The operations were carried out in acid solutions by zinc dust. In both cases the fumaroid form was obtained in the largest quantity (that is, 4 grams of the fumaroid form and 0·25 gram of the maleoid form). The two forms were separated from one another by means of their calcium salts.

As hæmopyrrole, on oxidation, yields an imide of a dibasic acid, in order to determine its constitution, synthetical imides were prepared. In addition to the imides of methylethylmaleic and methylpropylmaleic acids, there were also prepared diethylmaleimide and the imide of Δ^1-*cyclo*hexene-1 : 2-dicarboxylic acid, which could be derived from a hæmopyrrole with the constitution of a tetrahydro*iso*indoline, thus:



The diethylmaleic acid was prepared from citraconic acid, which reacts with its anhydride presumably according to the following equation: $C_5H_6O_4 + C_5H_4O_3 = C_8H_{10}O_3 + 2CO_2$. The imide prepared from this acid was an oil, boiling at 138—140°. Neither this nor the imide of Δ^1-*cyclo*hexene-1 : 2-dicarboxylic acid was identical with the oxidation product of hæmopyrrole. The latter was obtained from Δ^1-*cyclo*hexene-1 : 2-dicarboxylic acid by first heating it above its melting point (240°), and then heating the anhydride so formed with alcoholic ammonia, also by the distillation of the substance obtained by treating the anhydride with ammonia in alcoholic and ethereal solutions; the latter substance thus prepared was amorphous, and had a composition corresponding with the formula $C_8H_{14}O_3N_2$. The anhydrides of Δ^2-*cyclo*hexene-1 : 2-dicarboxylic acid, *trans*-Δ^4-*cyclo*hexene-1 : 2-dicarboxylic acid, and *cis*-Δ^4-*cyclo*hexene-1 : 2-dicarboxylic acid were also prepared by the Baeyer methods; from these, the corresponding imides were obtained, which do not agree in properties with the oxidation product of hæmopyrrole. These properties are indicated in the following table:

	Anhydride.	Imide.
Phthalic acid	m. p. 128°	233°
Δ^1-*cyclo*hexene-1 : 2-dicarboxylic acid	,, 73—74	169—170
Δ^2-*cyclo*hexene-1 : 2-dicarboxylic acid	,, 78—79	172—173
cis-Δ^4-*cyclo*hexene-1 : 2-dicarboxylic acid...	,, 59—60	?
trans-Δ^4-*cyclo*hexene-1 : 2-dicarboxylic acid	,, 140	232—233

Evidence is given as to the existence of two hæmopyrroles, obtainable by the reduction of hæmatin with hydriodic acid, one, an acid substance, which can be extracted from acid solutions with ether, and the other, a basic substance. An account is given of the attempts to prepare pure derivatives, and also of some oxidation experiments. A preliminary account of some oxidation experiments carried out with the non-volatile by-products in the hæmopyrrole preparation is also given, by means of which hæmatinic acid was obtained. S. B. S.

A New Method of Tanning. Louis Meunier and Alphonse Seyewetz (*Compt. rend.*, 1908, **146**, 987—989).—Hides are not greatly changed by quinol in the absence of oxygen, but, when oxygen and alkali are present, the fibre gradually becomes pink, then violet, and finally brown, and acquires perfect resistance to boiling water. The tanning depends on the formation of benzoquinone, and is also brought about by a solution of the latter substance; during the tanning process, the benzoquinone is again partly reduced to quinol. The explanation is sought in a reaction between benzoquinone and the amino-groups of the protein, similar to that between aniline and benzoquinone, which results in a condensation of aniline with part of the benzoquinone, and in the reduction of the rest of the benzoquinone to quinol. G. B.

Nucleic Acids. XIII. Phœbus A. Levene and John A. Mandel (*Biochem. Zeitsch.*, 1908, **10**, 215—220. Compare Abstr., 1907, i, 266).—A method is described of obtaining pure guanine from the cleavage products of nucleic acid. The cleavage is brought about by acetic acid in the presence of lead acetate at 150°. The lead is removed by sulphuric acid, the acetic acid by distillation under reduced pressure, and the purine bases are precipitated by silver sulphate and then treated in the usual way. Some experiments are also given on the determination of the proportion between purine and pyrimidine bases, but this matter is still being investigated.

W. D. H.

The Nucleo-protein of the Liver. I. Guanylic Acid. Phœbus A. Levene and John A. Mandel (*Biochem. Zeitsch.*, 1908, 10, 221—228).—A substance corresponding with Bang's β-guanylic acid was prepared from the liver. Its reactions were not, however, absolutely identical with Bang's acid, which was made from the pancreas. In elementary composition, the figures were fairly close. From it, guanine was prepared, but no adenine; the pyrimidine bases were absent. Hexoses were absent from the molecule; a pentose was obtained, but its identification was not very certain; glycerol was not obtained.

W. D. H.

Constitution of Thymonucleic Acid. Phœbus A. Levene and John A. Mandel (*Ber.*, 1908, 41, 1905—1909).—In continuation of an investigation of the intermediate products formed by the hydrolysis of nucleic acids (Abstr., 1904, ii, 955), it has been observed that, on hydrolysis with dilute mineral acids, thymonucleic acid yields, on the one hand, products containing carbohydrate groupings and traces of phosphoric acid, but without reducing action on Fehling's solution, and, on the other, substances which do not contain purine bases, but on further hydrolysis yield phosphoric acid, lævulic acid, and thymin. By hydrolysis of thymonucleic acid by 2% sulphuric acid at 150°, there has now been obtained an amorphous *barium thyminglucophosphate*, $C_{11}H_{15}O_{10}N_2PBa$, which, when heated with 25% sulphuric acid at 175°, yields thymin and lævulic and phosphoric acids. The composition of the thyminglucophosphoric acid is almost identical with that of heminucleic acid (Schmiedeberg, Abstr., 1900, i, 267; Alsberg, Abstr., 1904, i, 791), and may be considered to be a mononucleotide. It is suggested that the nucleic acids are composed of simpler complexes, the nucleotides, each formed of phosphoric acid, a carbohydrate, and a base, these complexes uniting to form polyphosphoric acids. The bases are combined with the carbohydrates, probably in the form of glucosides, somewhat according to the scheme:

$$\left.\begin{array}{r} C_5H_5ON_5\!:\!CH\cdot[CH\cdot OH]_4\cdot O\cdot PO(OH) \\ C_5H_5N_5\!:\!CH\cdot[CH\cdot OH]_4\cdot O\cdot PO(OH) \end{array}\right> O.$$

According to this view, the complex nucleic acids are constituted in the same manner as the simpler guanylic and inosic acids, but, whilst these readily yield free carbohydrates or reducing glucophosphoric acids when hydrolysed, the presence of the carbohydrate groups in the immediate products of the hydrolysis of thymonucleic acid can be detected only by the colour reactions with orcinol, or by hydrolysis to lævulic acid.

G. Y.

Adsorption of Ferments. Leonor Michaelis and M. Ehrenreich (*Biochem. Zeitsch.*, 1908, 10, 283—299).—The electrochemical nature of ferments is considered to be proved. Invertin and pepsin are adsorbed in all reactions by clay, and in none by kaolin; they therefore have the character of acids. In neutral and alkaline fluids, malt-diastase is not adsorbed by kaolin, but in acid fluids it is; it is therefore amphoteric, but with stronger acid than basic properties. Corresponding with this, it is completely adsorbed by clay when neutral or alkaline, and only incompletely when acid. Ptyalin and trypsin are also amphoteric, being adsorbed by both clay and kaolin under all conditions of reaction. W. D. H.

The Identity of Pepsin and Rennin. Olof Hammarsten (*Zeitsch. physiol. Chem.*, 1908, 56, 18—80).—A long critical and experimental examination of the much-debated point as to whether or not pepsin and rennin are identical. The conclusion reached is that they are not, and the most striking proof of this is that solutions of each ferment were prepared from which the other was absent. If lead acetate or, better, magnesium carbonate is added to the mixture, both ferments are precipitated, but the precipitate of pepsin is more insoluble and the ferment is destroyed; extracts of the precipitate then contain practically only rennin. If, on the other hand, the original mixture is heated to a little over 40°, the rennin is destroyed rapidly, but the pepsin is destroyed less rapidly, and so can be obtained free from rennin. W. D. H.

Systematic Investigation of Oxydases. Octave Dony-Hénault (*Bull. Acad. roy. Belg.*, 1908, 105—163. Compare Abstr., 1907, i, 1100).—The experimental methods used by Bertrand (Abstr., 1895, i, 385, 386; 1896, i, 534; ii, 61; 1897, i, 53; ii, 117, 338; 1898, i, 53; ii, 128; 1899, i, 313; 1904, i, 157) in his investigation of the ferment laccase of Japanese lac, and the conclusions this author draws from his results, are criticised, and evidence is brought forward in favour of the view that the oxidising action of laccase is really due, not to a specific enzyme, but to the presence of a manganous salt, the activity of which is stimulated by the action of hydroxyl ions.

When a solution containing a colloid and a manganous salt is precipitated by the addition of alcohol, the precipitate obtained contains some of all the constituents originally present in the solution, and this is the case even if the precipitation is repeated. Such precipitates exhibit feebly all the oxidising properties attributed to laccase and other oxidising ferments, and their activity can be greatly enhanced by the addition of minute traces of alkalis, so small as to be unrecognisable by the usual indicators. Bertrand's laccase is feebly alkaline, and always contains manganese, and its activity is practically paralysed in presence of acids. In view of these and other observations, it is contended that it is unnecessary to assume that Bertrand's laccase preparations, obtained by precipitating the latex of the lac tree by means of alcohol, contain any specific ferment, and that their oxidising action on quinol, pyrogallol, &c., is fully accounted for by the presence of an organic salt of manganese and the accidental presence of alkali. It is suggested, however, that these do not account for the oxidation of guaiacol by "laccase" and that some other constituent, possibly an iron salt, intervenes in this instance. The results of a number of quantitative experiments on the oxidation of quinol by manganous salts, showing the influence of concentration, time, temperature, and other factors on this action, are tabulated in the original. It is also shown that animal charcoal rapidly oxidises quinol to benzoquinone in presence of air. It is also pointed out that too much stress is often laid on the mere inhibition of catalytic activity by the application of heat, as an indication of the presence of enzymes. For example, "laccase" becomes inactive at 100°, but there is good reason to believe that, in presence of colloids, organic manganous salts would decompose at this temperature and lose their oxidising activity. The oxidation of quinol to benzoquinone by salts of mercury, nickel, and other metals is possibly also due to their action in presence of alkalis or like impurities. T. A. H.

The Occurrence of Anticatalase in the Animal Organism. Fr. Battelli and Lina Stern (*Biochem. Zeitsch.*, 1908, 10, 275—276). —Polemical against Vandevelde and de Waele (this vol., i, 491). The present authors use the prefix anti- in the same sense as it is employed in the words antipepsin, antitrypsin, &c. W. D. H.

Rôle of the Reductase in Alcoholic Fermentation. Wladimir N. Palladin (*Bull. Acad. Sci. St. Petersburg*, 1908, [iv], 8, 667—672 *).—It is shown that both vegetable and animal reductase are directly concerned in alcoholic fermentation. The reduction of sodium selenite and of methylene-blue by zymin is retarded greatly by the addition of dextrose, and to a less extent by sucrose and galactose, but glycerol, lactose, and mannitol hasten the process of reduction.

An analogy is drawn between these processes and the selective assimilation by fungi of the more nutritive of two substances in a mixture, and also of *d*- rather than *l*-tartaric acid by certain bacteria. Z. K.

The Properties of Yeast Juice; the Zymase Formation in Yeast. Edward Buchner and Fritz Klatte (*Biochem. Zeitsch.*, 1908, 9, 415—435).—Fresh yeast juice has but small optical rotation, varying in Munich yeast between + 0·12° and − 0·28° and in Berlin yeast between + 1·68° and 2·48°. This activity appears to depend on the glycogen (of which $[\alpha]_D = +196—213°$), for the rotation almost disappears on allowing the juice to ferment without addition of sugar. When sugar is added, the decrease in the dextrorotation does not correspond with its diminution as measured by collecting the carbon dioxide. In two cases, in spite of the disappearance of sugar, the rotation remained approximately constant. This phenomenon is possibly due to the concurrent formation of dextrorotatory polysaccharides. In the presence of disodium hydrogen phosphate, however, there was a decrease in the dextrorotation, which corresponded more nearly with the disappearance of the sugar.

Lange has shown that by keeping yeast for two hours in a solution containing 0·1% asparagine and 4% potassium phosphate, with or without the addition of 10% sucrose, the fermentative power can be increased. Further experiments have shown that this treatment causes a regeneration of the zymase, and that the increased power is not due to the formation of fresh enzyme. The asparagine, furthermore, plays a very subordinate part, and the regeneration is due mainly to the presence of potassium dihydrogen phosphate; the corresponding dipotassium salt does not possess the like power.

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* and *Zeitsch. physiol. Chem.*, 1908, 56, 81–88.

S. B. S.

The Alcoholic Ferment of Yeast-Juice. III. The Function of the Phosphates in the Fermentation of Dextrose by Yeast-Juice. Arthur Harden and William J. Young (*Proc. Roy. Soc.*, 1908, **80**, *B*, 299—311).—The addition of a phosphate to a fermenting mixture of dextrose and yeast-juice, not only produces a temporary acceleration in the rate of fermentation, but also an increased total fermentation. The last effect is due to the fact that the hexose phosphate formed during the period of temporary acceleration is continually hydrolysed by an enzyme with the production of free phosphate, which again enters into reaction and thus brings about fermentation. The reaction due to the phosphate can probably be represented as follows:

$$C_6H_{12}O_6 + 2R_2HPO_4 = 2CO_2 + 2C_2H_6O + C_6H_{10}O_4(PO_4R_2)_2 + 2H_2O.$$

This reaction is only realised in the presence of ferment and co-ferment, phosphate alone being unable to bring about fermentation in presence of ferment and dextrose (Abstr., 1907, i, 104). The hexose phosphate formed is gradually hydrolysed:

$$C_6H_{10}O_4(PO_4R_2)_2 + 2H_2O = C_6H_{12}O_6 + 2R_2HPO_4.$$

The conditions affecting this hydrolysis have been investigated; the rate at which it occurs, determines the rate of action when dextrose is fermented with yeast-juice. An optimum concentration of phosphate exists which produces a maximum initial rate of fermentation; an increase beyond this optimum diminishes the rate. S. B. S.

p-Dimethylaminophenylarsonic Acid (Dimethylatoxyl). August Michaelis (*Ber.*, 1908, **41**, 1514—1516).—*p*-Dimethylaminophenylarsonic acid, previously prepared by the action of mercuric oxide and water on *p*-dimethylaminophenylarsenious oxide (Abstr., 1902, i, 412), is now obtained by heating dimethylaniline with arsenic trichloride and treating the crude *p*-dimethylaminophenylarsenious oxide so formed with water, sodium hydroxide, and hydrogen peroxide, or by the action of methyl sulphate on aminophenylarsonic acid in sodium hydroxide solution. *p*-Dimethylaminophenylarsonic acid acid blackens when heated, and does not sublime as previously stated (*loc. cit.*). The *sodium* salt,

$$NMe_2{\cdot}C_6H_4{\cdot}As(OH){\cdot}ONa,5H_2O,$$

crystallises in leaflets. G. Y.

An Isomeric Aminophenylarsonic Acid. Alfred Bertheim (*Ber.*, 1908, **41**, 1655—1657).—The nitrophenylarsonic acid described by Michaelis and Loesner (Abstr., 1894, i, 187) may be reduced to the corresponding *aminophenylarsonic acid*, $NH_2{\cdot}C_6H_4{\cdot}AsO(OH)_2$, by means of hydrogen sulphide (compare Michaelis, preceding abstract), provided that, after treating the solution of the nitro-compound in ammonium hydroxide with hydrogen sulphide, the product obtained on evaporating to dryness is extracted with hydrochloric acid, the extract rendered alkaline with sodium hydroxide, and then treated with a solution of copper sulphate. The reduction may also be performed with sodium amalgam. Whether this substance, which is isomeric with *p*-aminophenylarsonic acid (compare Ehrlich and Bertheim, Abstr., 1907, i, 812), is an ortho- or meta-compound has not been determined, although the latter is more probable. It crystallises in colourless prisms, m. p. 214°. It does not couple with diazobenzene or diazosulphanilic acid, but does so with *p*-nitrodiazobenzene, yielding a yellow *dye*, dissolving in alkalis with a red colour. It may itself be diazotised, and then forms *azo-dyes* with amines and phenols, which are soluble in sodium carbonate. W. H. G.

Diazophenylarsonic Acid and its Products of Decomposition. Alfred Bertheim (*Ber.*, 1908, 41, 1853—1857).—*p*-Diazophenylarsonic acid (Ehrlich and Bertheim, Abstr., 1907, i, 812) undergoes the usual diazo-decomposition. On boiling in acid solution, it yields p-*hydroxyphenylarsonic acid*, $HO\cdot C_6H_4\cdot AsO(OH)_2$, crystallising from dilute alcohol in white needles containing $2\frac{1}{2}H_2O$. *p*-Ethoxyphenylarsonic (phenetylarsonic acid) is obtained by diazotising the base, dissolved in absolute alcohol by means of hydrogen chloride, with ethyl nitrite. It has m. p. 185° (Michaelis, Abstr., 1902, i, 413, gives 209—210°). By acting on the diazo-compound with sodium hypophosphite, phenylarsonic acid is obtained, m. p. 158—162° (Michaelis gives 158°), and, by treating with copper powder, *p-chlorophenylarsonic acid* is formed, of which the *barium* salt was analysed. Treatment of the diazo-solution with cuprous cyanide, and hydrolysis of the resulting *nitrile*, furnishes *p*-carboxyphenylarsonic acid. Arsenious carboxyphenyl iodide has m. p. 172° (La Coste, Abstr., 1881, 903, gives m. p. 153°). J. C. C.

Preparation of Acyl Derivatives of *p*-Aminophenylarsonic Acid. [Kuratorium der Georg und Franziska Speyerschen Studienstiftung] (D.R.-P. 191548).—Sodium *p*-aminophenylarsonate is readily acylated by the ordinary processes, and in this way the following derivatives have been obtained: p-*formylaminophenylarsonic acid*, slender needles, soluble in methyl alcohol or hot water, and p-*acetylaminophenylarsonic acid*, leaflets; the *phthalyl-*, *butyryl-*, *chloroacetyl-*, *benzoyl-*, and *malonyl-*p-*aminophenylarsonic acids* are similar compounds. The *carbonyl* derivative, $CO[NH\cdot C_6H_4\cdot AsO(OH)_2]_2$, was also prepared. G. T. M.

Some Homologues and Derivatives of Arsanilic Acid. I. Ludwig Benda and Robert Kuhn (*Ber.*, 1908, 41, 1672—1678. Compare Ehrlich and Bertheim, Abstr., 1907, i, 812; O. and R. Adler, this vol., i, 492).—Homologues of aniline not substituted in the para-position readily condense with arsenic acid when heated at 170—200°, yielding substituted arsanilic acids; at the same time, aromatic cacodylic acids of the type $AsO(\cdot Ar\cdot NH_2)_2\cdot OH$ are obtained as by-products. All the substituted arsanilic acids obtained give white silver salts. The amino-group may be acetylated and diazotised; the diazo-compounds couple with amines and phenols, yielding azo-dyes soluble in alkalis. The diazo-group is also readily replaceable by hydroxyl and halogens. The acetyl derivatives of the methyl homologues of arsanilic acid yield the corresponding carboxylic acids on oxidation.

6-*Aminotolyl*-3-*arsonic acid*, $NH_2\cdot C_6H_4\cdot AsO(OH)_2$, obtained from arsenic acid and *o*-toluidine, crystallises in hexagonal prisms, m. p. 195°; the *acetate*, $C_9H_{12}O_4NAs$, crystallises in brittle needles and prisms, decomposing at 306°.

5-*Aminotolyl*-2-*arsonic acid*, $C_7H_{10}O_3NAs$, from arsenic acid and *m*-toluidine, crystallises in long, rectangular prisms, m. p. 180°; the *acetate* forms prismatic crystals, decomposing above 240°.

5-*Amino*-p-*xylyl*-2-*arsonic acid*, $C_8H_{12}O_3NAs$, from *p*-xylidene and arsenic acid, crystallises with $1H_2O$ in compact, hexagonal plates; the anhydrous substance has m. p. 215°; the *acetate*, $C_{10}H_{14}O_4NAs$, forms compact, prismatic crystals, decomposing at 278°.

1-*Naphthylamine*-4-*arsonic acid*, $NH_2\cdot C_{10}H_6\cdot AsO(OH)_2$, from arsenic acid and α-naphthylamine, forms small prisms, m. p. 175°. 3-*Chloro*-4-*aminophenylarsonic acid*, $NH_2\cdot C_6H_3Cl\cdot AsO(OH)_2$, from *o*-chloroaniline and arsenic acid, forms white crystals, m. p. 305°. o-*Cresol*-5-*arsonic acid*, $C_6H_3Me(OH)\cdot AsO(OH)_2$, is prepared by diazotising 1-methyl-2:5-arsanilic acid and boiling the aqueous solution of the diazo-compound; it crystallises with $1H_2O$ in white prisms and needles, m. p. 180°; the anhydrous substance has m. p. 222°.

W. H. G.

The Magnesium Derivatives of the Aromatic Chloro-compounds. A. Hesse (D.R.-P. 189476).—In the Grignard reaction, chloro-derivatives behave quite differently from the bromo- and iodo- compounds, the latter readily react, giving rise both to alkyl and aryl magnesium halides, but aryl magnesium chlorides have not hitherto been produced by the ordinary methods. By the intervention of a more reactive alkyl halide, the reaction with magnesium may be started, and then this metal combines with the aromatic chloro-derivative.

Magnesium tolyl, *benzyl* or *cymyl chloride* can be produced by adding magnesium to an ethereal solution of ethyl bromide and then introducing chlorotoluene, benzyl chloride, or chlorocymene, or, conversely, the magnesium alkyl halide (from methyl bromide, ethyl iodide, &c) may be added to an ethereal solution of the aromatic chloro-derivative in the presence of the requisite amount of magnesium.

G. T. M.

Organic Chemistry.

Estimation of Active Hydrogen in Organic Compounds. Th. Zerewitinoff (*Ber.*, 1908, **41**, 2233—2243. Compare Abstr., 1907, ii, 509).—An extension of the method previously described to the determination of the number of replaceable hydrogen atoms in hydroxy-, thiol-, amino-, and imino-compounds. Frequently the results obtained are high, owing to the development of heat from the formation of the compound of pyridine and magnesium methiodide, and the further interaction of the pyridine and iodide with evolution of gas. The mixture is therefore cooled after the first evolution of gas has occurred. Care should also be taken that no barium oxide is introduced with the dry pyridine.

Ten hydroxy-compounds of the flavone type have been examined, and good results obtained even where the hydroxyl group is in the ortho-position; thus euxanthone is shown to contain two and hæmatoxylin five hydroxyl groups. The method also succeeds with mercaptans, such as the propyl, *iso*butyl, or phenyl derivatives, and with imido-compounds, such as succinimide, oxanilide, or phthalimide (compare Hibbert and Sudborough, Trans., 1904, **85**, 933). The acid amides, like acetamide, react in the cold with one mol. of magnesium methiodide, and on heating at 85° with another mol.; the error due to the action of the pyridine is estimated by carrying out a blank experiment. Aldehyde-ammonia is shown in this way to have three active hydrogen atoms, two of which react in the cold. Carbamide and thiocarbamide have only three instead of four active hydrogen atoms, and phenylcarbamide, phenylthiocarbamide, and menthonesemicarbazone have two such hydrogen atoms; in all these cases the compound contains two amino- or one amino- and one imino-groups attached to the same carbon atom.

The reaction has been applied to tautomeric compounds, such as acetylacetone and ethyl acetoacetate, and at 100° these possess one active hydrogen atom; malonic acid contains three replaceable hydrogen atoms. W. R.

Methylethyl*iso*butylmethane [βδ-Dimethylhexane]. Latham Clarke (*J. Amer. Chem. Soc.*, 1908, **30**, 1144—1151).—In continuation of the work on the octanes (Abstr., 1907, i, 169), βδ-dimethylhexane has been synthesised by two different methods.

When methyl *iso*butyl ketone, prepared by the hydrolysis of ethyl *iso*propylacetoacetate, is treated with magnesium ethyl bromide, *βδ-dimethyl-δ-hexanol*, $CHMe_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH_2Me$, b. p. 151°/768 mm., is produced. On converting this compound into the corresponding iodide and reducing the latter with zinc and hydrochloric acid, *βδ-dimethylhexane*, $CH_2Me{\cdot}CHMe{\cdot}CH_2{\cdot}CHMe_2$, b. p. 109·8—110°/762 mm., is obtained as an odourless, mobile liquid with D_{15}^{15} 0·7083, and n_D^{25} 1·3986.

When *ethyl* sec.*-butylacetoacetate*, b. p. 210—211°/762 mm., is

hydrolysed with potassium hydroxide, *δ-methyl-β-hexanone*,
$CH_3\cdot CO\cdot CH_2\cdot CHMe\cdot CH_2Me$,
b. p. 139°/762 mm., is produced, and on treatment with magnesium methyl iodide is converted into *βδ-dimethyl-β-hexanol*,
$OH\cdot CMe_2\cdot CH_2\cdot CHMe\cdot CH_2Me$,
b. p. 150—150·5°/766 mm. If this carbinol is converted into the iodide and the latter reduced with zinc and hydrochloric acid, βδ-dimethylhexane is obtained, identical with the compound prepared by the first method.

β-Chloro-δ-methyl-$\Delta^{\alpha\beta}$-amylene, $CHMe_2\cdot CH_2\cdot CCl\colon CH_2$, b. p. 102·5°/760 mm., obtained by the action of phosphorus pentachloride on methyl *iso*butyl ketone, is a colourless, mobile liquid, and on oxidation with potassium permanganate yields *iso*valeric acid. E. G.

Behaviour of Trimethylene Dibromide towards Zinc Dust and Acetic Acid. NICOLAI ZELINSKY and N. SCHLESINGER (*Ber.*, 1908, **41**, 2429—2431).—After pointing out that no reaction occurs between glacial acetic acid and zinc dust, the authors state that carefully-dried trimethylene dibromide, glacial acetic acid, and zinc dust evolve with extreme slowness a gas which is found to be hydrogen, showing that a trace of water must still have been present. When 50% acetic acid is used, the gas which is evolved more rapidly, but still only slowly, proves to be *cyclo*propane, and not propane, which would be expected to be obtained. If the dibromide is gradually heated with glacial acetic acid, zinc dust, and concentrated hydrochloric or hydrobromic acid, the issuing gas consists of hydrogen free from hydrocarbon. As a result of these experiments, the authors consider that the first step in the reduction of trimethylene dibromide is the formation of a zinc additive compound, which is then decomposed by water; the latter must be present in not inconsiderable amount for the reduction to take place:
(*a*) $C_3H_6Br_2 + Zn = C_3H_6Br_2Zn$; (*b*) $C_3H_6Br_2Zn + H_2O =$
$OH\cdot C_3H_6ZnBr + HBr$; (*c*) $OH\cdot C_3H_6ZnBr = C_3H_6 + Zn(OH)Br$.
C. S.

Action of Metallic Oxides on Primary Alcohols. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, **146**, 1376—1378).—The oxides examined fall into four classes: (1) those which undergo no reduction and which exert no appreciable effect on primary alcohols below 400°. This group includes titanium dioxide and the oxides of calcium, barium, strontium, magnesium, and silicon; (2) those rapidly reduced either to the metal or to a lower oxide; (3) oxides which are not reduced, but which decompose the alcohols catalytically, giving rise to hydrogen and an aldehyde, or to water and an ethylenic hydrocarbon, or to a mixture of aldehyde and hydrocarbon; (4) those oxides which are slowly reduced and at the same time exert a catalytic action. W. O. W.

Action of Metallic Oxides on the Primary Alcohols (Case of the Reducible Oxides). PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1908, **147**, 16—18).—As already stated (preceding abstract), primary alcohols are oxidised when passed over many oxides heated below 400°. These oxides may be divided into four classes.

The simplest case is that in which the oxidation is limited to the formation of aldehyde and water, the oxide having no action on the aldehyde and the reduced oxide or metal having no catalytic power. The oxides of antimony and bismuth act in this way.

In the case of the more readily reducible oxides, the aldehyde formed is partly oxidised either to the corresponding acid or to carbon dioxide and water. Mercuric oxide is reduced by ethyl alcohol vapour at 150°, giving acetaldehyde and a large proportion of carbon dioxide, but not acetic acid. Manganese dioxide at 200° is reduced by ethyl alcohol to the sesquioxide, acetaldehyde being formed; at 250°, however, the sesquioxide formed is reduced, carbon dioxide and acetic acid being formed in addition to the aldehyde.

The third and largest class of oxides contains those of which the reduced metal or lower oxide has a catalytic action on the alcohol, the catalytic reaction being superposed on the initial oxidation. The oxides of nickel, cobalt, lead (PbO_2, Pb_3O_4, PbO), and copper (Cu_2O and CuO) at 350° belong to this class; the reduced metals have a dehydrogenating action on ethyl alcohol, giving acetaldehyde and hydrogen. In the case of nickel and lead oxides, but not with the copper oxides, acetic acid is produced. Manganese sesquioxide at 350° is slowly reduced by ethyl alcohol to the pale green manganous oxide, which decomposes ethyl alcohol into aldehyde and hydrogen. On the other hand, the yellow tungsten trioxide, WO_3, at 350° is readily reduced by ethyl alcohol vapour, giving a blue intermediate oxide, which has a powerful dehydrating catalytic action, thus causing the formation of increasing amounts of ethylene besides the acetaldehyde, carbon dioxide, and acetic acid initially produced. Other oxides are reduced by alcohol vapour to lower non-reducible oxides, which are both dehydrating and dehydrogenating catalysts. Thus uranium trioxide, UO_3, is reduced to UO_2, and V_2O_5 to V_2O_3, by alcohol vapour, giving aldehyde and carbon dioxide, whilst the reduced oxides act on further quantities of alcohol, giving aldehyde, hydrogen, ethylene, and water. In this class, the completion of the reduction is indicated by the disappearance of carbon dioxide in the gases produced.

The fourth class of oxides contains those which have themselves a catalytic action on alcohols. The latter is readily observed if the reduction is slow, but if this is rapid it is perceived only with difficulty. Thus ferric oxide, like alumina, is a dehydrating catalyst towards ethyl alcohol vapour, giving at 340° a mixture of ethylene and water, and being reduced to ferrous oxide and metallic iron. The latter, being a dehydrogenating catalyst, decomposes the alcohol into aldehyde and hydrogen. From this it follows that the proportion of ethylene gradually diminishes. Cadmium and stannous oxides, which are reduced very slowly by alcohol vapour at 340°, similarly act as dehydrogenating catalysts. E. H.

Decomposition of Alcohols under the Catalytic Influence of Charcoal (Braise). Georges Lemoine (*Compt. rend.*, 1908, **146**, 1360—1366. Compare Senderens, Abstr., 1907, ii, 248).—The author has examined the gaseous and liquid products formed when alcohols in the state of vapour are passed over "quenched charcoal" (Braise de boulanger) heated to a temperature not exceeding 400° and usually below 385°. Methyl, ethyl, *n*-propyl, *iso*propyl, *iso*butyl, and amyl alcohols were treated in this way, and it was found in each case that the liquid product consisted of unaltered alcohol and substances having the reducing properties of aldehydes. Complete analyses of the gaseous products have been made, and it is found that hydrogen is always an important constituent of the mixture, except in the case of *iso*propyl alcohol, which becomes dehydrated with formation of trimethylene.

W. O. W.

αα-Dialkyl-β-keto-alcohols. Transformation by Dehydration. Edmond E. Blaise and I. Herman (*Compt. rend.*, 1908, **146**, 1326—1328).—The transformation of ethyl hydroxypivalyl ketone, $OH\cdot CH_2\cdot CMe_2\cdot COEt$, into *iso*propyl methylvinyl ketone,

$$CH_2\colon CMe\cdot CO\cdot CHMe_2,$$

by the action of alkalis can be explained by a migration of the primary alcohol group followed by dehydration, thus:

$$OH\cdot CH_2\cdot CMe_2\cdot CO\cdot CH_2Me \longrightarrow CHMe_2\cdot CO\cdot CHMe\cdot CH_2\cdot OH \longrightarrow CHMe_2\cdot CO\cdot CMe\colon CH_2,$$

or the dehydration may occur first and then a migration of the methyl group: $OH\cdot CH_2\cdot CMe_2\cdot CO\cdot CH_2Me \longrightarrow {>}CH\cdot CMe_2\cdot CO\cdot CH_2Me \longrightarrow CH_2\colon CMe\cdot CO\cdot CHMe_2$. From the second hypothesis, it would be expected that the action of dehydrating agents would be similar to that of alkalis. When ethyl hydroxypivalyl ketone is treated with phosphoric oxide, however, the product is not *iso*propyl methylvinyl ketone, but another unsaturated ketone. The latter is identical with the ketone formed when β-acetoxy-α-methylbutyryl chloride is treated with ethyl zinc iodide and the product saponified and dehydrated:

$$OAc\cdot CHMe\cdot CHMe\cdot COCl + ZnIEt \longrightarrow OAc\cdot CHMe\cdot CHMe\cdot COEt \longrightarrow OH\cdot CHMe\cdot CHMe\cdot COEt \longrightarrow CHMe\colon CMe\cdot COEt.$$

It is therefore *ethyl tiglyl ketone*, $CHMe\colon CMe\cdot COEt$, has b. p. 52°/15 mm., and gives a p-*nitrophenylhydrazone*, m. p. 134°, and a *semicarbazone*, m. p. 161—162°. Its formation by dehydration of ethyl hydroxypivalyl ketone is to be represented thus:

$$OH\cdot CH_2\cdot CMe_2\cdot COEt \longrightarrow {>}CH\cdot CMe_2\cdot COEt \longrightarrow CHMe\colon CMe\cdot COEt.$$

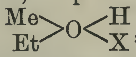
Ethyl tiglyl ketone is also formed by the action of tiglyl chloride on ethyl zinc iodide.

The conclusion is drawn that the action of alkalis on ethyl hydroxypivalyl ketone is represented by the first of the above schemes, the dehydration being preceded by the transposition.

E. H.

Basic Properties of Oxygen. Douglas McIntosh (*J. Amer. Chem. Soc.*, 1908, **30**, 1097—1104).—Baeyer and Villiger (Abstr., 1901, i, 658; 1902, i, 112, 355), in studying the basic properties of oxygen, have prepared a large number of compounds of organic substances with ferrocyanic acid. In order that the acid should be attached to the oxygen base in the simplest possible way, 4 mols. of the latter should unite with 1 mol. of the former, but in many of the compounds described this ratio does not exist. For this reason, and also since water may have been present in the salts, an investigation has been made of the compounds of ferrocyanic acid with methyl and ethyl alcohols, acetone, and ether. A study of the vapour pressure of the products obtained by the absorption of ether and acetone by the acid has shown that they are not quadrivalent oxygen compounds, but solid solutions. With ethyl alcohol, a crystalline *compound*, m. p. −45°, containing 35·7% of the acid was obtained, and with methyl alcohol a *compound*, m. p. −33°, containing 37% of the acid. These compounds contain about 10 mols. of the alcohol to one of the acid, and are much more complex than those obtained by Baeyer and Villiger; their properties indicate that they are molecular compounds in which the alcohols are present as alcohol of crystallisation.

Acetic acid dissolves in liquid hydrogen bromide and hydrogen iodide with development of heat and formation of crystalline substances. The hydrogen bromide *compound*, m. p. 5°, contains 46—49% HBr. Tschitschibabin (Abstr., 1907, i, 276) has described a compound, $2C_2H_4O_2,HBr$, m. p. 7—8°. The hydrogen iodide *compound*, m. p. −50°, contains 59—70% HI.

Methyl ethyl ether unites with liquid hydrogen bromide and hydrogen iodide to form white, crystalline *compounds*, MeEtO,HBr and MeEtO,HI, m. p. −30° and −22°. If these compounds have the constitution  ${}^{\mathrm{Me}}_{\mathrm{Et}}{>}\mathrm{O}{<}{}^{\mathrm{H}}_{\mathrm{X}}$, the oxygen atom is asymmetric. Attempts to separate them into optically active isomerides were not successful.

E. G.

Preparation of Methyl Sulphate. SOCIÉTÉ ANONYME DES PRODUITS CHIMIQUES DE FONTAINES IN LYON-MONPLAISIR (D.R.-P. 193830).—Methyl sulphate is conveniently prepared by adding chlorosulphonic acid (24 kilos.) to a mixture of 6·5 kilos. of methyl alcohol (90%) and 20 kilos. of carbon tetrachloride. After boiling off the diluent, the methyl sulphate is distilled under reduced pressure. A similar result is obtained on adding sulphur trioxide to the mixture of methyl alcohol and carbon tetrachloride.

G. T. M.

Reduction of Alkyl Nitrates to Nitrites in Alkaline Solution. AUGUST GUTMANN (*Ber.*, 1908, 41, 2052—2056).—Nitrite and arsenate are formed when an alcoholic solution of amyl or ethyl nitrate is heated in a pressure flask at 100° with a solution of arsenious oxide in sodium hydroxide.

The author draws the conclusion that the presence of these products points to the intermediate formation of ethyl hydroperoxide: $NO_2{\cdot}OEt + NaOH \longrightarrow NO_2Na + EtO{\cdot}OH$ and $EtO{\cdot}OH + As(ONa)_3 \longrightarrow EtOH + AsO(ONa)_3$.

Potassium cyanide and sulphide also reduce ethyl and amyl nitrates yielding potassium nitrite, potassium thiocyanate, and the alcohol. In this reaction, the author assumes the intermediate formation of ethyl hydropersulphide: $NO_2{\cdot}OEt + KSH \longrightarrow KNO_2 + EtO{\cdot}SH$ and

$EtO{\cdot}SH + KCN \longrightarrow EtOH + KCNS$. The sulphide solution used should be free from polysulphides and thiosulphate.

The reaction may be used in testing for alkyl nitrates in presence of the corresponding nitrites, as the latter do not give the yellow coloration and do not produce thiocyanates. J. J. S.

Character of the Compound formed by the Addition of Ammonia to Ethyl Phosphite-platochloride. Charles H. Herty and R. O. E. Davis (*J. Amer. Chem. Soc.*, 1908, **30**, 1084—1089).—Rosenheim and Levy (Abstr., 1905, i, 183) have found that when dry ammonia is passed into a solution of triethyl phosphite-platochloride in benzene, the compound $\left[Pt\genfrac{}{}{0pt}{}{(NH_3)_2}{P(OEt)_3}\right]_2Cl_4$ separates in white crystals, and that this salt is hydrolysed by water, forming an acid solution which exhibits abnormal molecular conductivity. The present authors, although following Rosenheim's method as closely as possible, have been unable to prepare this substance, but have obtained only the normal *salt*, $\left[\begin{matrix}Cl\\ Pt(NH_3)_2\\ P(OEt)_3\end{matrix}\right]Cl$, which forms white crystals, and dissolves in water to give a neutral solution. Determinations of the molecular conductivity at 25° are recorded, and agree closely with the values obtained by Werner for all di-ionic complex ammonia compounds. E. G.

Molybdenum Compounds of Lecithin. Richard Ehrenfeld (*Zeitsch. physiol. Chem.*, 1908, **56**, 89—94).—Alcoholic lecithin solutions, when precipitated in the cold with an alcoholic nitric acid solution of ammonium molybdate, yield a substance, $10MoO_3$, 3 mols. of lecithin, when the lecithin is in excess, and $2MoO_3$, 1 mol. of lecithin, when the precipitant is in excess. A substance, $5[(NH_7)_6Mo_7O_{24}]$, 1 mol. of lecithin, is precipitated by an aqueous ammonium molybdate solution when there is a large excess of lecithin. G. B.

Preparation of Concentrated Formic Acid. Chemische Fabrik Grünau, Landshoff & Meyer (D.R.-P. 193509).—Although highly concentrated sulphuric or phosphoric acid acts destructively on formic acid, yet their acid salts decompose formates without exhibiting this action, and sodium hydrogen sulphate, when intimately mixed with dry sodium formate and heated in a retort, gives rise to 97—98% formic acid. G. T. M.

Hydrates of the Fatty Acids. D. E. Tsakalotos (*Compt. rend.*, 1908, **146**, 1272—1274. Compare this vol., i, 498).—The constitution of the molecular combinations of acetic, propionic, and butyric acids with water is considered to be best represented by the formula $\genfrac{}{}{0pt}{}{H}{R{\cdot}CO}{>}O{:}O{<}\genfrac{}{}{0pt}{}{H}{H}$.

The coefficients of viscosity of mixtures of formic acid with *m*-cresol are only slightly lower than the coefficients calculated from the rule of mixtures. Formic acid therefore shows less tendency than its homologues to form additive products with phenols. W. O. W.

Preparation of Phosphoric Esters from Phosphoric Oxide and the Diglycerides of Fatty Acids and their Bromo- and Iodo-derivatives. Ferdinand Ulzer and J. Batik (D.R.-P. 193189).—*Glyceryl distearophosphate*, $PO(HO)_2 \cdot O \cdot C_3H_5(OCOC_{17}H_{35})_2$, m. p. 58°, is obtained in almost quantitative yield by mixing together phosphoric oxide and melted distearin and slowly adding water. The corresponding oleyl derivative is oily. Glyceryl dibromodistearophosphate is a brown, viscid mass, having an acid number 109·3 and a saponification number 218·3. Other similar glycerides are referred to in the patent, all of which are obtained by the same general method of adding the requisite amount of water to an intimate mixture of phosphoric oxide and to the diglyceride of a fatty acid. G. T. M.

Catalytic Actions of Colloidal Metals of the Platinum Group. III. Reduction Catalysis with Colloidal Palladium and Platinum. Carl Paal and Josef Gerum (*Ber.*, 1908, 41, 2273—2282. Compare Abstr., 1905, ii, 397, 533; 1907, ii, 559; Willstätter, this vol., i, 383).—When the investigation was extended to unsaturated acids, it was found that the method applicable for the reduction of nitrobenzene did not lead to the conversion of sodium fumarate into succinate, but that when the salt and the hydrosol of palladium hydride are left together in a closed vessel filled with hydrogen, the gas is quickly absorbed.

In this way, fumaric, maleic, and cinnamic acids, as well as methyl cinnamate, have been reduced to the corresponding saturated acid and the rate of absorption measured. As a general rule, there is a little more hydrogen absorbed than that required by theory; this may be due to the metal, but in one case an aldehyde-like odour was observed, so that the reduction may proceed further than the acid. Palladium-black may be used, as also colloidal platinum, but the action is slower. W. R.

Catalytic Actions of Colloidal Metals of the Platinum Group. IV. Reduction Catalysis with Colloidal Palladium. Carl Paal and Karl Roth (*Ber.*, 1908, 41, 2282—2291. Compare preceding abstract).—The reduction of oleic acid to stearic acid has been carried out at the ordinary temperature by Fokin (Abstr., 1907, i, 819), and it may be accomplished by using sodium oleate and palladium hydrosol, the yield of pure stearic acid obtained being 60%. The method has been extended to the reduction of fats, the Hübl iodine value being used to determine percentage of unsaturated acids before and after. The fats used were castor oil, olive oil, and cod-liver oil. A quantitative yield of saturated fats was obtained from the castor oil in the form of a white, hard, crystalline mass, sintering at 77°, m. p. 81°. Although three times the quantity of hydrogen required was absorbed by the olive oil, the reduction was not quite complete (iodine value before, 81—82; after, 9); the tallow has m. p. 47°. Cod-liver oil was very nearly completely reduced; the product obtained was crystalline, m. p. 43—45°. The method therefore appears to be the only one yet discovered for reducing the unsaturated glycerides in a fat at the ordinary temperature. W. R.

Preparation of Glycollic Acid by the Electrolytic Reduction of Oxalic Acid. DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT (D.R.-P. 194038).—When oxalic acid is electrolysed in moderately concentrated sulphuric acid contained in an electrolytic cell fitted with a diaphragm and electrodes having a high supertension, a good yield of glycollic acid is produced. The following are details of this reduction. Cathode compartment, 700 parts of crystallised oxalic acid, 1100 parts of concentrated sulphuric acid, and 3300 parts of water; lead cathodes, current density 25 to 250 amperes per square metre; anode compartment, 30% sulphuric acid with an intermediate cell containing acid of the same strength. The temperature of the cathode solution was maintained above 25° throughout the electrolysis.

G. T. M.

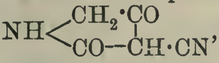
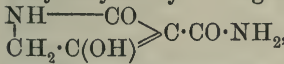
Ethyl Chlorocyanoacetoacetate and its Derivatives. ERICH BENARY (*Ber.*, 1908, **41**, 2399—2411).—Whilst chloroacetyl chloride reacts with ethyl sodiomalonate to form mainly ethyl tetrone-4-carboxylate (Abstr., 1907, i, 381), its behaviour with ethyl sodiocyanoacetate in dry ether leads smoothly to the formation of *ethyl γ-chloro-α-cyanoacetoacetate*, $CH_2Cl\cdot CO\cdot CH(CN)\cdot CO_2Et$, m. p. 42—43°, which crystallises in colourless needles, has an acid reaction, develops a red coloration with ferric chloride, and is best purified by means of the green, crystalline *copper* salt, m. p. 171—172° (decomp.). The corresponding *methyl* ester, $C_6H_6O_3NCl$, m. p. 72—73°, forms a *copper* salt, which decomposes at 188—189°. Bromoacetyl bromide reacts with ethyl sodiocyanoacetate in a similar manner, yielding *ethyl γ-bromo-α-cyanoacetoacetate*, $C_7H_8O_3NBr$, m. p. 59—61°, which has properties similar to those of the chlorinated compound; the *copper* salt has m. p. 163—164° (decomp.).

The dry silver salt of ethyl chlorocyanoacetoacetate reacts with ethereal ethyl iodide to form *ethyl γ-chloro-α-cyano-β-ethoxycrotonate*, $CH_2Cl\cdot C(OEt){:}C(CN)\cdot CO_2Et$, m. p. 93—94°, which forms colourless needles, does not give a coloration with ferric chloride, and yields with alcoholic ammonia, *ethyl γ-chloro-β-amino-α-cyanocrotonate*,

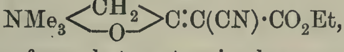
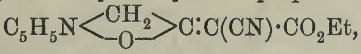
$$CH_2Cl\cdot C(NH_2){:}C(CN)\cdot CO_2Et,$$

m. p. 128—129°, in which the position of the amino-group is determined by the fact that the same compound is obtained by the action of ammonia on ethyl γ-chloro-α-cyano-β-methoxycrotonate.

Ethyl chlorocyanoacetoacetate reacts with potassium cyanide in aqueous solution at 50—60° to form *ethyl αγ-dicyanoacetoacetate*, $CN\cdot CH_2\cdot CO\cdot CH(CN)\cdot CO_2Et$, m. p. 87—89°, in which the presence of the reactive methylene group enables the compound to condense with benzaldehyde and cinnamaldehyde, yielding the *benzylidene* and the *cinnamylidene* derivatives, the m. p. of which are 145—146° and 159—160° respectively; the latter is orange-coloured and the former yellow, having acid properties, and developing a blood-red coloration with ferric chloride.

The course of the reaction between ethyl chlorocyanoacetoacetate and ammonia or organic bases in aqueous solution at the ordinary temperature depends on the base. Whilst with tertiary amines betaines are formed, and with ammonia a pyrrolidone derivative, secondary amines cause a simple replacement of the halogen, and primary amines, in addition, the formation of pyrrolidone derivatives; the production of the heterocyclic compound, however, does not occur in the case of primary aromatic amines. The addition of sodium hydroxide facilitates the preceding reactions. 4-*Cyano*-3 : 5-*diketopyrrolidine*,  $NH<\begin{matrix}CH_2\cdot CO\\ CO\text{--}CH\cdot CN\end{matrix}$, begins to decompose at 210° and melts completely at 220—221°; the *silver* salt, $C_5H_3O_2N_2Ag$, crystallises in small needles. The compound is not attacked by boiling baryta, but is hydrolysed by boiling 30% potassium hydroxide, yielding the *amide*,  $\begin{matrix}NH\text{——}CO\\ CH_2\cdot C(OH)\end{matrix}\!>\!C\cdot CO\cdot NH_2$, which decomposes at 215°. *Ethyl α-cyano-γ-ethylaminoacetoacetate*, $NHEt\cdot CH_2\cdot CO\cdot CH(CN)\cdot CO_2Et$, m. p. 225°, decomposition commencing at 215°, separates from hot water in long needles, reduces Fehling's solution, and forms a *sodium* salt and a *hydrochloride*, which decomposes at 173—174°. 4-*Cyano*-3 : 5-*diketo*-1-*ethylpyrrolidine*, obtained from the filtrate in the preceding preparation, darkens at 200°, and decomposes and melts completely at 228°; the *ammonium* salt has m. p. 194—195°. *Ethyl α-cyano-γ-anilinoacetoacetate*, $NHPh\cdot CH_2\cdot CO\cdot CH(CN)\cdot CO_2Et$, decomposes at 212—213°; the *hydrochloride* has m. p. 182—183° (decomp.). *Ethyl α-cyano-γ-o-methoxyphenylaminoacetoacetate*,

$$OMe\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot CH(CN)\cdot CO_2Et,$$

m. p. 207—208°, crystallises in white needles. *Ethyl α-cyano-γ-piperidinoacetoacetate*, $C_5NH_{10}\cdot CH_2\cdot CO\cdot CH(CN)\cdot CO_2Et$, decomposes at 215—216°, and forms a *hydrochloride*, m. p. 159—160° (decomp.), a *sodium* salt, which darkens at 300° and has m. p. 310° (decomp.), and a *copper* salt, which decomposes at 226—227°. *Ethyl α-cyano-γ-dimethylaminoacetoacetate*, m. p. 208—209° (decomp.), forms a *hydrochloride*, m. p. 143—144°, and a violet *copper* salt, which decomposes at 226—227°. The *betaine* of ethyl α-cyano-γ-trimethylaminoacetoacetate,  $NMe_3<\begin{matrix}CH_2\\ O\end{matrix}>C\colon C(CN)\cdot CO_2Et$, m. p. 205—206° (decomp.), separates from hot water in hexagonal plates, and has a neutral reaction, bitter taste, and very feebly basic properties. The analogous *pyridine derivative*,  $C_5H_5N<\begin{matrix}CH_2\\ O\end{matrix}>C\colon C(CN)\cdot CO_2Et$, decomposes at 250—251°. All the preceding substances, obtained by the action of bases on ethyl chlorocyanoacetoacetate, reduce warm ammoniacal silver solutions and develop a red coloration with ferric chloride; the pyrrolidine derivatives are strongly acidic, whilst the others have a neutral reaction and very feeble acid properties.

Ethyl chlorocyanoacetoacetate and phenylhydrazine in aqueous solution yield Rupe's α-phenylhydrazino-β-acetylphenylhydrazine (Abstr., 1898, i, 572). C. S.

Potassium Ammonium Oxalate. Phillippe Barbier (*Bull. Soc. chim.*, 1908, [iv], 3, 725—726).—Anhydrous potassium ammonium oxalate separates in colourless, slender needles when a concentrated solution of potassium oxalate is added to a saturated solution of

ammonium carbonate to which a small quantity of ammonia solution has been added. When potassium oxalate is replaced by sodium oxalate, no separation of the corresponding sodium ammonium oxalate occurs.
T. A. H.

Tautomerism of Succinyl Chloride. Richard Meyer and Karl Marx (*Ber.*, 1908, **41**, 2459—2471. Compare Meyer and Jugilewitsch, Abstr., 1897, i, 350).—From the investigation of Auger (Abstr., 1888, 952), succinyl chloride is apparently a mixture of the symmetrical with the asymmetrical compound; nevertheless, on treating succinyl chloride with an alcohol, the same ester is obtained as by acting on silver succinate with the corresponding alkyl iodide. In no case was an isomeride isolated from the product formed from the succinyl chloride; this fact speaks for the tautomeric character of succinyl chloride (compare Emery, Abstr., 1890, 236).

The following new esters of succinic and dibromosuccinic acid have been prepared:

Cetyl succinate, $C_2H_4(CO_2{\cdot}C_{16}H_{33})_2$, crystallises in small, glistening leaflets, m. p. 58°. p-*Nitrobenzyl succinate*, $C_2H_4(CO_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, crystallises in slender needles, m. p. 90°; the corresponding o-*nitrobenzyl* ester has m. p. 104—105°. *Cetyl dibromosuccinate*,

$$C_2H_2Br_2(CO_2{\cdot}C_{16}H_{33})_2,$$

has m. p. 36—37°. *Benzyl dibromosuccinate*, $C_2H_2Br_2(CO_2{\cdot}CH_2Ph)_2$, forms short, stout crystals, m. p. 92—93°.

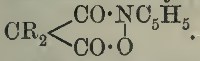
When succinyl chloride is heated with bromine at 140—150° in a flask fitted with a reflux condenser, the principal product formed is succinyl bromide; this reacts with benzene and aluminium chloride, yielding an *additive* product which is decomposed by water with the formation of dibromosuccinophenone (compare Paal and Schulze, Abstr., 1902, i, 228).

The fraction, b. p. 115—127°, obtained during the fractionation of the impure succinyl bromide, prepared as just described, yields on treatment with benzene and aluminium chloride a mixture of dibromosuccinophenone and a *substance* crystallising in colourless leaflets, m. p. 97—100°.

Dibromosuccinophenone yields on treatment with phenylhydrazine a *substance* which probably has the formula $C_2H_2(CPh{:}N{\cdot}NHPh)_2$; it softens at about 60°, and decomposes at 100°. Similarly, a *substance*, $C_2H_2(CPh{:}N{\cdot}NPh{\cdot}CH_2Ph)_2$, is obtained by acting on the ketone with *as*-phenylbenzylhydrazine; it crystallises in colourless needles, m. p. 109°.
W. H. G.

Ketens. X. Malonic Semichloride, Malonic Anhydride, and its Transformation into Keten. Hermann Staudinger and E. Ott (*Ber.*, 1908, **41**, 2208—2217. Compare this vol., i, 411).—In attempting to prepare malonyl chloride by acting on an ethereal solution of malonic acid with thionyl chloride, a product was obtained which proved to be malonic semichloride. It was thought possible that by acting on this compound with tertiary bases, the hitherto unknown unimolecular anhydride of malonic acid would be obtained.

Instead, however, *additive* products were formed of the type $C_5NH_5Cl\cdot CO\cdot CR_2\cdot CO_2H,NC_5H_5$. The product obtained from malonic semichloride decomposes when warmed, yielding a tarry substance; the products from the semichlorides of dimethyl- and diethylmalonic acid yield amorphous *substances* having the constitution



$$CR_2<\begin{matrix}CO\cdot NC_5H_5\\ |\\ CO\cdot O\end{matrix}.$$

When heated under reduced pressure, malonic semichloride yields acetyl chloride and carbon dioxide; the corresponding diethyl derivative yields α-ethylbutyryl chloride and carbon dioxide, whilst dimethylmalonic semichloride yields *iso*butyryl chloride, carbon dioxide, and dimethylmalonic anhydride. The latter compound was found to be identical with that described by Einhorn (this vol., i, 312) as a duodecimolecular anhydride of dimethylmalonic acid. It is insoluble in most solvents; in others it dissolves with decomposition, consequently the mol. wt. cannot be determined. The slight depression of the freezing point observed by Einhorn, which led to the belief in the existence of a duodecimolecular form, was undoubtedly due to the presence of impurity. The same also applies to diethylmalonic anhydride (Abstr., 1906, i, 398).

Both anhydrides, although undoubtedly highly polymerised, react as if unimolecular; thus, both compounds decompose when heated, yielding ketens: $CR_2(CO)_2O \longrightarrow CO_2 + CR_2{:}CO$.

Malonic semichloride, $COCl\cdot CH_2\cdot CO_2H$, crystallises in small needles, m. p. about 65° (decomp.). It readily decomposes both at the ordinary temperature and when heated. *Dimethylmalonic semichloride*, $C_5H_7O_3Cl$, forms compact crystals, m. p. about 64—65° (decomp.), having a characteristic odour. The corresponding *diethyl* compound was obtained as an oil, which could not be solidified.

Dimethylmalonic anhydride (compare Einhorn, *loc. cit.*) is a slightly grey powder, which when rapidly heated decomposes at 170—175°. It decomposes when heated under a pressure of 12 mm. at 160—180°, yielding dimethylketen (compare Staudinger and Klever, Abstr., 1906, i, 234). The latter compound distils with slight decomposition at 34°/750 mm.; it has m. p. $-97{\cdot}5°$, b. p. 48·5°/12 mm.

Diethylketen, $CEt_2{:}CO$, prepared from diethylmalonic anhydride, is a liquid, b. p. 91—92°/749 mm., which solidifies to a yellow, crystalline mass at the temperature of liquid air. It is slightly more yellow than the dimethyl compound. W. H. G.

Ferrous and Ferric Double Salts of Polybasic Acids. A. Scholz (*Monatsh.*, 1908, 29, 439—450).—Whilst ferrous salts are usually green and ferric salts yellow, Eder and Valenta (Abstr., 1881, 713) found that oxalic acid forms a yellow potassium ferrous, but a green potassium ferric, salt. These results have now been confirmed, and double ferrous and ferric salts of malonic acid prepared and found also to have the usual colours reversed.

Potassium and *ammonium ferrous malonates*, $FeM'_2(C_3H_2O_4)_2,2H_2O$ ($M' = K$ or NH_3), are prepared from ferrous iodide and potassium and ammonium malonates, and form yellow crystals which oxidise rapidly on exposure to air. A sodium ferrous malonate could not be prepared.

Potassium, sodium, and *ammoninm ferric malonates,*

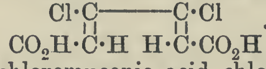
$$Fe_2M'_6(C_3H_2O_4)_6,4H_2O\ (M' = K,\ Na,\ \text{or}\ NH_3),$$

are prepared from ferric hydroxide, malonic acid, and potassium, sodium, or ammonium malonate, and form emerald-green crystals which are readily soluble in water.

Attempts to prepare double salts of succinic, glutaric, and fumaric acids led to the formation of the known basic ferric salts; maleic acid yields a *basic ferric* salt, $C_4H_2O_4Fe\cdot OH$. G. Y.

Muconic Acid Derivatives. Constitution of Dichloromuconic Acid. DAN RADULESCU (*Chem. Zentr.*, 1908, i, 1832—1833; from *Bul. Soc. Stiinte Bucuresti*, 1907, **16**, 191—206).—In view of the fact that when ethyl dichloromuconate is treated with sodium ethoxide a disodium compound is produced, and that Canizzaro's reaction yields diacetyl, the constitution of this substance must be

$$CO_2H\cdot CH{:}CCl\cdot CCl{:}CH\cdot CO_2H,$$

and the stability of the free acid, acid chloride, and amide points to the configuration  $\begin{array}{c} Cl\cdot C\text{———}C\cdot Cl \\ \|\qquad\quad\ \| \\ CO_2H\cdot C\cdot H\ \ H\cdot C\cdot CO_2H \end{array}$. Details are given for the preparation of dichloromuconic acid chloride from a mixture of dry muconic acid and phosphorus pentachloride. It is a colourless, tasteless, and odourless substance, giving an *amide* which does not melt below 210°. An apparatus is described enabling the preparation and filtration of this ester to be performed in an atmosphere of an inert gas. J. V. E.

Preparation of Methylenecitric Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 193767. Compare Abstr., 1904, i, 649).—The reactions formerly employed in preparing methylenecitric acid are more or less reversible, owing to the presence of water among the products. The condensation becomes complete when methylene derivatives, such as methylene sulphate, methyl methylenediacetate, or chloromethyl acetate, are employed which can condense without the elimination of water.

Anhydrous citric acid, when heated at 140—150° with the calculated amount of methyl methylenediacetate and a few drops of concentrated sulphuric acid, yields pure methylenecitric acid, which is crystallised from boiling water. When methylene sulphate is employed, the condensation is effected in the presence of sodium acetate or glacial acetic acid. A good yield of methylenecitric acid is obtained when trioxymethylene condenses either with acetylcitric acid or with citric acid in the presence of acid chlorides or anhydrides. G. T. M.

Xanthic Acid. MANFRED RAGG (*Chem. Zeit.*, 1908, **32**, 630—631, 654—656, 677—679).—In the reaction of a copper salt with an ethylxanthate, a brownish-black precipitate is obtained, the colour of which soon changes to yellow. It has frequently been suggested that cupric xanthate is first formed, which then is decomposed with formation of the cuprous salt. The author has re-investigated this question, and comes to the following conclusions: (1) The yellow precipitate just referred to is cuprous xanthate. (2) Cupric xanthate is not formed in the reaction. The evanescent, brownish-black precipitate also formed initially consists mainly of cupric thiocarbonate. (3) This is due to the fact that in the preparation of the xanthate a certain proportion of thiocarbonate is also formed, owing to a reaction between alkali hydroxides and xanthates. (4) The author shows that the reaction between an alkali xanthate and a cupric salt yields cuprous xanthate and dixanthogen, as shown by the equation

$$4OEt\cdot CS\cdot SNa + 2CuSO_4 = Cu_2(S\cdot CS\cdot OEt)_2 + S_2(CS\cdot OEt)_2 + 2Na_2SO_4.$$

J. V. E.

Preparation of Dithioglycollic Acid and Arylthioglycollic Acids. KALLE & Co. (D.R.-P. 194039, 194040).—When aqueous solutions of sodium disulphide and sodium chloroacetate are mixed in the cold, there is little or no deposition of sulphur. The mixture becomes warm, and, after heating to boiling, the solution contains sodium dithioglycollate.

When thioglycollic acid is treated with a soluble diazo-salt, a diazo-derivative, $R\cdot N_2\cdot S\cdot CH_2\cdot CO_2H$, of this acid is produced as an insoluble, crystalline precipitate, which, on heating, loses nitrogen and gives rise to an arylthioglycollic [arylthiolacetic] acid, $R\cdot S\cdot CH_2\cdot CO_2H$. The following have been prepared: *phenylthiolacetic acid*, $SPh\cdot CH_2\cdot CO_2H$, colourless needles, m. p. 117°; p-*tolylthiolacetic acid*,

$$C_7H_7\cdot S\cdot CH_2\cdot CO_2H,$$

needles, m. p. 93°; o-*carboxyphenylthiolacetic acid*,

$$CO_2H\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H,$$

obtained from diazotised anthranilic acid; *a-naphthylthiolacetic acid*, white needles. G. T. M.

Preparation of Formaldehydesulphoxylate. BADISCHE ANILIN- & SODA FABRIK (D.R.-P. 194052).—Normal zinc sulphite, in aqueous solution, when treated successively with zinc dust and formaldehyde at 100° furnishes a sparingly soluble basic zinc formaldehydesulphoxylate, $ZnSO_3 + Zn + CH_2O + H_2O = CH_2O\cdot ZnSO_2 + Zn(OH)_2$. Ammonium sulphite, when treated similarly, furnishes ammonium formaldehydesulphoxylate. G. T. M.

Inversion of Sucrose by Invertase. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1908, **30**, 1160—1166).—O'Sullivan and Tompson (Trans., 1890, **51**, 834) have found that the inversion of sucrose by invertase is a unimolecular reaction, and have shown that the results of other observers who held the opposite view were vitiated by a systematic error in their polarimetric measurements. This error is due to the fact that the dextrose formed is initially in a birotatory state, and therefore the optical activity of a solution undergoing inversion does not indicate the amount of inversion which has taken place. If, however, alkali hydroxide is added to the solution and the optical activity is allowed to become constant, the true amount of inversion which has taken place at the moment of adding the alkali is accurately indicated.

In the present paper, an account is given of a study of this question, and data are quoted which show that the inversion of sucrose by acids is a unimolecular reaction, even in its first stages, and that the polarimetric measurement of the inversion of sucrose by invertase involves a large source of error which can be obviated by adding alkali hydroxide to the solution before each reading. When this source of error is eliminated, as was done by O'Sullivan and Tompson, the inversion follows the unimolecular order. E. G.

Formation of Molasses. Sergius Lebedeff (*Zeitsch. Ver. deut. Zuckerind.*, 1908, 599—621).—In order to trace the causes of molasses formation, the effect of some non-sugar constituents of molasses on the solubility of sucrose has been determined. Betaine has a slight salting-out effect at 30°, but at higher temperatures (50—70°) it increases the solubility of sucrose, and potassium glutamate (the other chief non-sugar constituent of molasses) increases the solubility of sucrose both at low and at higher temperatures. G. B.

Action of Formaldehyde on Starch. Albert Reichard (*Chem. Zentr.*, 1908, i, 1834—1835; from *Zeitsch. ges. Brauwesen*, 1908, **31**, 161—163).—Solutions of formaldehyde lower the temperature at which starch gelatinises. In the same space of time, a 2% formaldehyde solution of starch was completely gelatinised at 59°, and a 37% solution at 49°. If left a sufficiently long time, gelatinisation is completed at the ordinary temperature. J. V. E.

Gum of the Almond Tree. R. Huerre (*J. Pharm. Chim.*, 1908, [vi], **27**, 561—569).—This gum differs from that of the closely-related apricot and plum trees in containing a small proportion of matter soluble in water (10—20% instead of 80—90%). Nevertheless, there is a close chemical relationship, all three consisting largely of pentosans, yielding arabinose on hydrolysis. From the almond tree gum, galactose has now, in addition, been isolated. G. B.

Decomposition Curves of some Nitrocelluloses of American Manufacture. Oswin W. Willcox (*Zeitsch. angew. Chem.*, 1908, **21**, 1407—1411).—During an investigation of the stability of ordinary collodion wool by Obermüller's method (Abstr., 1905, ii, 291), the author has found that the amount of decomposition in a definite interval of time is greater when the gaseous decomposition products are left in contact with the sample during the preceding interval than when they are removed. From an examination of the curves, it appears that a given sample of nitrocellulose, when heated at 140°, has a characteristic decomposition pressure; as the heating is continued, a new component or phase is produced, which reinforces the previous one by its decomposition pressure; the pressure increase then remains more or less constant until a new phase is again produced, and so the process repeats itself. P. H.

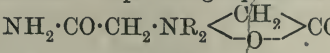
Preparation of the Alkyl Halides of Dialkylaminodimethylethylcarbinol and their Benzoyl Derivatives. J. D. Riedel (D.R.-P. 195813).—The dialkylaminodimethylethylcarbinols and their benzoyl derivatives, when treated with alkyl halides, furnish quaternary salts which have valuable therapeutic properties.

Trimethyl-β-hydroxy-β-methylbutylammonium bromide,
$$HO\cdot CMeEt\cdot CH_2\cdot NMe_3Br,$$
colourless spicules, m. p. 168—169°, is produced by adding methyl bromide to dimethylaminodimethylethylcarbinol; its *benzoyl* derivative (stovaine methobromide) forms colourless needles.

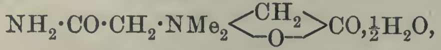
Trimethyl-β-hydroxy-β-methylbutylammonium iodide,
$$HO\cdot CMeEt\cdot CH_2\cdot NMe_3I,$$
colourless prisms, m. p. 123—125°, and its *benzoyl* derivative, needles, m. p. 169—170°. *Dimethylethyl-β-hydroxy-β-methylbutylammonium bromide*, $HO\cdot CMeEt\cdot CH_2\cdot NMe_2EtBr$, its *benzoyl* derivative, the corresponding quaternary *ethiodide*, and its *benzoyl* derivative, needles, m. p. 155—157°, are prepared similarly. G. T. M.

Synthesis of Alanine and α-Aminobutyric Acid. Nicolai D. Zelinsky and Georg Stadnikoff (*Ber.*, 1908, 41, 2061—2063).—α-Aminopropionitrile hydrochloride is obtained in a 23%, together with alanine in a 40%, yield from acetaldehyde by the authors' method for the synthesis of aminonitriles. In the same manner, α-aminobutyronitrile hydrochloride is obtained in a 25%, together with α-aminobutyric acid in a 29·4%, yield from propaldehyde. In support of the authors' view of the mechanism of the reaction, experiments are quoted showing that α-aminophenylacetonitrile and α-amino*cyclo*hexylacetonitrile are formed from benzaldehyde and *cyclo*hexanone respectively only in the presence of water. G. Y.

A New Synthesis of *iso*Leucine. Walther Brasch and Ernst Friedmann (*Beitr. chem. Physiol. Path.*, 1908, 11, 376—380).—*sec.*-Butylmalonic acid, $CHMeEt\cdot CH(CO_2H)_2$, yields on bromination the α-derivative, $CHMeEt\cdot CBr(CO_2H)_2$, which, when heated, is converted into α-bromo-β-methylvaleric acid, $CHMeEt\cdot CHBr\cdot CO_2H$; this, when left in contact with concentrated ammonia solution, yields α-amino-β-methylvaleric acid, $CHMeEt\cdot CH(NH_2)\cdot CO_2H$, or *iso*leucine. S. B. S.

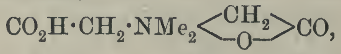
Betainecarboxylic Acids and Betainecarboxyamides. Julius von Braun (*Ber.*, 1908, 41, 2123—2129).—Bromoacetonitrile unites with tertiary aminoacetonitriles which do not contain an aromatic group to form quaternary ammonium salts,
$$NR_2Br(CH_2\cdot CN)_2.$$
When these are shaken with silver hydroxide, not only is the bromine replaced by hydroxyl, but at least one of the cyanomethyl groups undergoes change, and on removing silver from the solution with hydrogen sulphide and evaporating, quantitative yields of betainecarboxylamides,  $NH_2\cdot CO\cdot CH_2\cdot NR_2{<}\genfrac{}{}{0pt}{}{CH_2}{O}{>}CO$, are obtained. On hydrolysis, these are converted into the corresponding betainecarboxylic acids.

s-*Di-ω-cyanotetramethylammonium bromide*, $NMe_2Br(CH_2\cdot CN)_2$, prepared from dimethylaminoacetonitrile and bromoacetonitrile in the cold, forms glistening crystals, m. p. 135° (decomp.), this with silver hydroxide yields *betainecarboxylamide*,

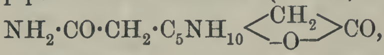


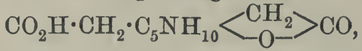
$$NH_2\cdot CO\cdot CH_2\cdot NMe_2{<}\substack{CH_2\\ -O-}{>}CO,\tfrac{1}{2}H_2O,$$

white powder, m. p. 122°, and this on hydrolysis with hydrochloric acid furnishes the *chloride*, $NMe_2Cl(CH_2\cdot CO_2H)_2$, white, crystalline powder, m. p. 207°, which, on treatment with silver hydroxide, gives *betainecarboxylic acid*,



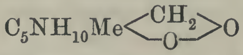
$$CO_2H\cdot CH_2\cdot NMe_2{<}\substack{CH_2\\ -O-}{>}CO,$$

white, crystalline powder, m. p. 245°. Similarly, biscyanomethylpiperidinium bromide (Abstr., 1907, i, 899) gives the *compound*,  $NH_2\cdot CO\cdot CH_2\cdot C_5NH_{10}{<}\substack{CH_2\\ -O-}{>}CO$, white powder, m. p. 230°, which, on hydrolysis, yields the corresponding *acid*,



$$CO_2H\cdot CH_2\cdot C_5NH_{10}{<}\substack{CH_2\\ -O-}{>}CO,$$

white powder, m. p. 249°; the *chloride*, $C_9H_{16}O_4NCl,2H_2O$, crystallises in rosettes of needles, m. p. 137° (decomp.); the anhydrous salt has m. p. 200°; the *bromide*, $C_9H_{16}O_4NBr,2H_2O$, crystallises in shining needles, m. p. 147—148°.

The compound  $C_5NH_{10}Me{<}\substack{CH_2\\ -O-}{>}O$ (Klages and Margolinsky, Abstr., 1904, i, 145) was prepared as follows: ethyl iodomethylpiperidiniumacetate (Wedekind and Oechslen, Abstr., 1902, i, 392) is converted into *ethyl chloromethylpiperidiniumacetate*,

$$C_5NH_{10}MeCl\cdot CH_2\cdot CO_2Et,$$

m. p. 189°, which gives a *platinichloride*, small, yellowish-red crystals, m. p. 225°, and, on treatment with hydrochloric acid, furnishes the required compound. The *chloride*, $C_5NH_{10}MeCl\cdot CH_2\cdot CO_2H$, has m. p. 213° (decomp.), and the *platinichloride* forms small, reddish-yellow crystals, m. p. 219°.

J. C. C.

***N*-Methylol Compounds of Acid Amides. II.** ALFRED EINHORN [and, in part, RICHARD FEIBELMANN, MAX GÖTTLER, ALEXANDER HAMBURGER, and EDUARD SPRÖNGERTS] (*Annalen*, 1908, **361**, 113—165. Compare Abstr., 1906, i, 245).—The *N*-methylol compounds of propionamide, *iso*butyramide, and dipropylacetamide have been prepared in amplification of the earlier paper. *N*-Methylolpropionamide, $CH_2Me\cdot CO\cdot NH\cdot CH_2\cdot OH$, is readily converted by alkalis at the ordinary temperature into *N*-methylolmethylenebispropionamide, $OH\cdot CH_2\cdot N(CO\cdot CH_2Me)\cdot CH_2\cdot NH\cdot CO\cdot CH_2Me$, or, when heated gently with acids, into methylenebispropionamide,

$$CH_2(NH\cdot CO\cdot CH_2Me)_2,$$

whilst on oxidation with chromic acid and sulphuric acid, it yields formylpropionamide, $CHO\cdot NH\cdot CO\cdot CH_2Me$. As with benzoylethylamide, attempts to prepare an *N*-methylol derivative of *iso*valerylethylamide have been unsuccessful. Urethane forms an *N*-methylol compound, $OH\cdot CH_2\cdot NH\cdot CO_2Et$, which behaves in the same manner as

N-methylolpropionamide, being converted by alkalis into *N*-methylolmethylenebisurethane, $OH\cdot CH_2\cdot N(CO_2Et)\cdot CH_2\cdot NH\cdot CO_2Et$, and by acids into methylenebisurethane (Conrad and Hock, Abstr., 1903, i, 605).

Whilst carbamide forms mono- and di-methylol derivatives (this vol., i, 141), a methylolethylcarbamide could not be obtained, but in its place is formed *N*-methylolmethylenebisethylcarbamide,

$$OH\cdot CH_2\cdot N(CO\cdot NHEt)\cdot CH_2\cdot NH\cdot CO\cdot NHEt.$$

Both dimethylcarbamides, on the other hand, yield monomethylol compounds, $NMe_2\cdot CO\cdot NH\cdot CH_2\cdot OH$ and $NHMe\cdot CO\cdot NMe\cdot CH_2\cdot OH$ respectively. This is remarkable, as monoalkylamides do not form methylol compounds. In acid solution, the dimethylcarbamides yield methylene derivatives, $CH_2(NH\cdot CO\cdot NMe_2)_2$ and

$$CH_2(NMe\cdot CO\cdot NHMe)_2.$$

Triethylcarbamide does not form a methylol derivative; this and the fact that *s*-dimethylcarbamide forms a mono-, but not a di-, methylol derivative may be looked upon as evidence in favour of the ψ constitution for carbamides, $OH\cdot C(NEt)\cdot NEt_2$ and $OH\cdot C(NMe)\cdot NHMe$. Like other acid amides, carbamide forms condensation products,

$$CO(NH\cdot CH_2\cdot NR_2)_2,$$

with formaldehyde and secondary bases.

Also the amides of hydroxy-carboxylic acids form *N*-methylol compounds; these contain one methylol for each amide group; lactic acid yields *N*-methylol-lactamide, $OH\cdot CHMe\cdot CO\cdot NH\cdot CH_2\cdot OH$; tartramide yields di-*N*-methyloltartramide,

$$OH\cdot CH_2\cdot NH\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot NH\cdot CH_2\cdot OH,$$

and citramide, a tri-*N*-methylol compound,

$$OH\cdot CH_2\cdot NH\cdot C(OH)(CH_2\cdot CO\cdot NH\cdot CH_2\cdot OH)_2.$$

N-Methylol-lactamide and *N*-methylolmandelamide yield dibenzoyl derivatives in which the methylol hydroxyl, as well as that of the hydroxy-acid, is benzoylated. Methylol compounds of the amides of quinoline-6-carboxylic acid and camphocarboxylic acid are described.

N-Methylolpropionamide, $C_4H_9O_2N$, prepared in a 90% yield from propionamide and formaldehyde in presence of barium hydroxide, crystallises in colourless prisms, m. p. 64°, is hygroscopic, and when heated evolves formaldehyde. N-*Methylolmethylenebispropionamide*, $C_8H_{16}O_3N_2$, crystallises in rhomboids, m. p. 76—77°, does not evolve formaldehyde when boiled with water, and reduces Tollens's silver solution more slowly than the preceding substance. *Methylenebispropionamide*, $C_7H_{14}O_2N_2$, crystallises in needles, m. p. 201°, and remains unchanged when boiled with potassium chromate and sulphuric acid or when heated with bromine. N-*Formylpropionamide*, $CH_2Me\cdot CO\cdot NH\cdot CHO$, formed by oxidation of N-methylolpropionamide with chromic acid in sulphuric acid solution, crystallises in prismatic needles, m. p. 65°, decomposes when heated, and yields formylphenylhydrazide, m. p. 142°, when boiled with alcoholic phenylhydrazine.

N-*Methylol*iso*butyramide*, $CHMe_2\cdot CO\cdot NH\cdot CH_2\cdot OH$, crystallises in needles, m. p. 77°.

α-Ethylbutyramide is best prepared by treating diethylmalonic acid with phosphorus trichloride, and the resulting ethylbutyryl chloride with ammonia in ethereal solution. *Methylenebis-α-ethylbutyramide*, $CH_2(NH\cdot CO\cdot CHEt_2)_2$, prepared by the action of hydrochloric acid on equal amounts of α-ethylbutyramide and its *N*-methylol derivative (*loc. cit.*), forms needles, m. p. 235°. *α-Ethylbutyryldiethylglycylmethylenediamine*, $CHEt_2\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NEt_2$, formed by the action of *N*-methylol-α-ethylbutyramide on diethylglycylamide in concentrated sulphuric acid solution, crystallises in prismatic leaflets, m. p. 78—79°, and has very weak basic properties.

N-*Methylol-α-propylvaleramide*, $CHPr_2\cdot CO\cdot NH\cdot CH_2\cdot OH$, formed from α-propylvaleramide and formaldehyde, crystallises in needles, m. p. 117°, evolves formaldehyde when heated, reduces Tollens's silver solution in a few minutes, and differs from the methylol derivatives of other amides of the fatty series by its insolubility in water.

iso*Valerylethylamide*, $CH_2Pr^{\beta}\cdot CO\cdot NHEt$, prepared by the action of *iso*valeryl chloride on ethylamine and sodium hydroxide, has m. p. 20—30°, b. p. 121°/20 mm.

The action of formaldehyde and barium hydroxide on urethane leads to the formation of N-*methylolurethane*, $C_4H_9O_3N$, which is obtained in colourless prisms, m. p. 53°; it evolves formaldehyde when heated alone or in aqueous solution, and yields methylenebisurethane when treated with dilute hydrochloric acid. N-*Methylolmethylenebisurethane*, $C_8H_{16}O_5N_2$, crystallises from benzene in prisms, m. p. 68—69°, evolves formaldehyde when heated, and reduces silver solutions slowly.

Methylolcarbamide has m. p. 111° (116°: this vol., i, 142), and when treated with dilute hydrochloric acid forms di-*N*-methylolcarbamide or, on prolonged treatment, an amorphous *substance*, decomp. 260°. The action of concentrated hydrochloric acid on di-*N*-methylolcarbamide leads to the formation of a *substance*, $C_{18}H_{33}O_{12}N_{13}$, which crystallises in needles, not melted at 250°, and forms two *hydrochlorides*, crystallising from dilute hydrochloric acid in leaflets and from concentrated hydrochloric acid in strongly refracting, rhombic prisms respectively.

N-*Methylolmethylenebisethylcarbamide*, $C_8H_{18}O_3N_4$, prepared by gently heating ethylcarbamide with formaldehyde and barium hydroxide, crystallises in needles, m. p. 168—170° (decomp.), and evolves formaldehyde when heated. *Methylenebisethylcarbamide*,

$$CH_2(NH\cdot CO\cdot NHEt)_2,$$

formed by the action of concentrated hydrochloric acid on formaldehyde and ethylcarbamide, crystallises in small needles, m. p. 204°, and yields a *picrate*, crystallising in reddish-yellow needles, m. p. 115—116°.

N-*Methylol*-as-*dimethylcarbamide*, $C_4H_{10}O_2N_2$, prepared from *as*-dimethylcarbamide, crystallises in plates from alcohol or from ethyl acetate in needles, m. p. 110°, and evolves formaldehyde when heated. *Methylenebis*-as-*dimethylcarbamide*, $C_7H_{16}O_2N_4$, formed from *as*-dimethylcarbamide and formaldehyde in concentrated hydrochloric acid solution, crystallises in rhombic prisms, m. p. 183·5—184°.

N-*Methylol*-s-*dimethylcarbamide* crystallises in prisms, m. p. 92°, is hygroscopic, reduces silver solutions fairly rapidly, and evolves formaldehyde when heated. *Methylenebis-*s*-dimethylcarbamide* crystallises from chloroform-ethyl acetate in prisms, m. p. 149—151°.

Condensation Products of Carbamide, Formaldehyde, and Secondary Bases.—s-*Tetraethyldiaminodimethylcarbamide*, $CO(NH{\cdot}CH_2{\cdot}NEt_2)_2$, prepared by heating carbamide with formaldehyde and diethylamine in aqueous solution, is obtained in a 35% yield as an oil, which decomposes on distillation in a vacuum. The *picrate*, $C_{23}H_{32}O_{15}N_{10}$, has m. p. 145—147°. s-*Dipiperidyldimethylcarbamide*,

$$CO(NH{\cdot}CH_2{\cdot}C_5NH_{10})_2,$$

prepared from carbamide, piperidine, and formaldehyde in a 60% yield, crystallises from ethyl acetate in needles, m. p. 136°.

N-*Methylol Compounds of Hydroxy-acid Amides.*—N-*Methylollactamide*, $C_4H_9O_3N$, prepared by the action of formaldehyde and barium hydroxide on lactamide, crystallises from alcohol in colourless pyramids, m. p. 82—84°, and evolves formaldehyde when heated. The *dibenzoyl* derivative, $OBz{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OBz$, formed by the action of benzoyl chloride on methylol-lactamide in pyridine solution, crystallises in needles, m. p. 124°. *Benzoyl-lactamide*,

$$OBz{\cdot}CHMe{\cdot}CO{\cdot}NH_2,$$

formed from lactamide by Schotten-Baumann's method, crystallises in needles, m. p. 115°.

iso*Valeryl-lactamide*, $C_4H_9{\cdot}CO{\cdot}O{\cdot}CHMe{\cdot}CO{\cdot}NH_2$, formed by the action of *iso*valeryl chloride on lactamide in pyridine solution, is obtained as a deliquescent mass or as a colourless oil, b. p. 157—158° in a vacuum.

Di-N-*methyloltartramide*, $C_6H_{12}O_6N_2$, from tartramide in a 70% yield, forms colourless crystals, m. p. 166°, and evolves formaldehyde when heated. When boiled with diethylamine in alcoholic solution, it forms *tetraethyldiaminodimethyltartramide*,

$$C_2H_2(OH)_2(CO{\cdot}NH{\cdot}CH_2{\cdot}NEt_2)_2,$$

which is obtained as an oil. The *dipicrate*, $C_{26}H_{36}O_{18}N_{10}$, forms yellow needles or leaflets, m. p. 155°. *Dibenzoyltartramide*,

$$NH_2{\cdot}CO{\cdot}CH(OBz){\cdot}CH(OBz){\cdot}CO{\cdot}NH_2,$$

formed by the Schotten-Baumann method from tartramide, crystallises in needles, m. p. 240°.

Tri-N-*methylolcitramide*, $C_9H_{17}O_7N_3$, forms colourless prisms, m. p. 149—161° (decomp.), and evolves formaldehyde when heated.

N-*Methylolmandelamide*, $OH{\cdot}CHPh{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OH$, forms colourless crystals, m. p. 73—81° (decomp.), and evolves formaldehyde when heated. The *dibenzoyl* derivative, $OBz{\cdot}CHPh{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OBz$, formed from the methylol compound in pyridine solution, crystallises in slightly red needles, m. p. 110—115°. *Diethylaminomethylmandelamide*, $OH{\cdot}CHPh{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}NEt_2$, prepared by boiling mandelamide, diethylamine, and formaldehyde in molecular proportions in alcoholic solution, is a basic oil; the *hydrochloride*, $C_{13}H_{20}O_2N_2,HCl$, forms needles, m. p. 155°. *Piperidylmethylmandelamide*,

$$OH{\cdot}CHPh{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}C_5NH_{10},$$

crystallises in colourless needles, m. p. 133—134°; the *hydrochloride*, $C_{14}H_{20}O_2N_2,HCl$, forms needles, m. p. 188°.

Catecholdiacetamide (Carter and Lawrence, Trans., 1900, **77**, 1225) was prepared by boiling catechol with chloroacetamide, sodium ethoxide, and sodium iodide in alcoholic solution; when treated with formaldehyde and potassium carbonate, it forms *di-*N*-methylolcatecholdiacetamide*, $C_6H_4(O{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OH)_2$, which separates in spherical crystals, m. p. 136—137°.

Resorcinoldiacetamide, prepared in the same manner as catecholdiacetamide, reacts with formaldehyde and potassium carbonate, forming *di-*N*-methylolresorcinoldiacetamide*, $C_{12}H_{16}O_6N_2$, which crystallises in microscopic needles, m. p. 192° (decomp.).

Additive Products of Halogenoacetamides and their Methylol Compounds with Hexamethylenetetramine.—The following additive compounds are described, $N_4(CH_2)_6{\cdot}R$.

R = Chloroacetamide: needles, m. p. 160° (decomp.); R = bromoacetamide: white needles, m. p. 170—171° (decomp.); R = iodoacetamide: leaflets, m. p. 166—167° (decomp.); R = methylolchloroacetamide: needles, m. p. 152° (decomp.); R = methylolbromoacetamide: needles, m. p. 155—158° (decomp.); R = methyloliodoacetamide: stellate needles, m. p. 150° (decomp.).

N*-Methylol Compounds of Amides of Quinoline-*6*-carboxylic and Camphocarboxylic Acids.*—*Quinoline-*6*-carboxylamide*, $C_{10}H_8ON_2$, prepared by the action of concentrated sulphuric acid on the corresponding nitrile, crystallises in yellow leaflets, m. p. 174°. The *ethiodide*, $C_{12}H_{13}ON_2I$, forms red or greenish-yellow crystals, m. p. 220° (partial decomp.). *Quinoline-*6*-carboxylmethylolamide*, $C_9H_6N{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OH$, prepared by the action of formaldehyde and potassium carbonate on the amide, forms colourless crystals, m. p. 179°, and evolves formaldehyde when heated. *Quinoline-*6*-carboxylpiperidylmethylamide*, formed from the amide, piperidine, and formaldehyde, crystallises in needles, m. p. 98°. The *hydrochloride*, $C_{16}H_{19}ON_3,HCl$, forms colourless crystals, m. p. 192°, and is neutral in aqueous solution.

Camphocarboxylamide, $C_{10}H_{15}O{\cdot}CO{\cdot}NH_2$, prepared by the action of alcoholic ammonia on the ethyl ester at 140—150°, crystallises in colourless leaflets, m. p. 116—117°, and forms a *di-*N*-methylol* derivative, $C_{10}H_{15}O{\cdot}CO{\cdot}N(CH_2{\cdot}OH)_2$, which crystallises in colourless needles, m. p. 152—153°, and evolves formaldehyde when heated. It yields a *dibenzoyl* derivative, $C_{10}H_{15}O{\cdot}CO{\cdot}N(CH_2OBz)_2$, microscopic crystals, m. p. 95°. *Diethylaminoethyl camphocarboxylate*,

$$C_{10}H_{15}O{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2,$$

is formed by prolonged action of hydrogen chloride on diethylaminoethyl alcohol and camphocarboxylic acid in chloroform solution at the ordinary temperature; it crystallises from acetone in needles, m. p. 153° (decomp.). *Chloroethyl camphocarboxylate*, $C_{13}H_{19}O_3Cl$, formed in the same manner from the acid and chlorohydrin, is obtained as a colourless liquid, b. p. 190—191°/15 mm., having an odour of camphor. The *diethylamide*, $C_{10}H_{15}O{\cdot}CO{\cdot}NEt_2$, prepared by heating the ethyl ester with diethylamine at 110—120°, crystallises in colourless leaflets, m. p. 60—61°. The *piperidide*, $C_{10}H_{15}O{\cdot}CO{\cdot}C_5NH_{10}$, crystallises in colourless leaflets, m. p. 101°.

Action of Methylolchloroacetamide on β-Naphthol.—The action of methylolchloroacetamide on β-naphthol in alcoholic hydrogen chloride solution leads to the formation of 2*-hydroxy-*1*-naphthylcarbinylchloro-*

acetamide, $OH\cdot C_{10}H_6\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, which crystallises in colourless needles, m. p. 132°, and on hydrolysis with aqueous alcoholic hydrochloric acid yields 2-hydroxy-1-naphthabenzylamine (Betti, Abstr., 1906, i, 653). 2-*Methoxy*-1-*naphthylcarbinylchloroacetamide*,

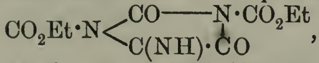
$$OMe\cdot C_{10}H_6\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl,$$

formed from the hydroxy-compound by the action of methyl sulphate and potassium hydroxide, crystallises in needles, m. p. 170°, and on hydrolysis with boiling alcoholic hydrogen chloride yields 2-*methoxy*-1-*naphthylcarbinylamine*, $OMe\cdot C_{10}H_6\cdot CH_2\cdot NH_2$, crystallising in needles, m. p. about 100°; the *hydrochloride*, m. p. 233° (decomp.); the *hydrobromide*, $C_{12}H_{13}ON,HBr$, m. p. 242° (decomp.). The action of sodium nitrite on the hydrochloride leads to the formation of a *nitroso*-derivative of the corresponding alcohol, $C_{12}H_{11}O_3N$, which separates from alcohol in crystals, m. p. 112°. G. Y.

Carbethoxycarbimide. II. OTTO DIELS and ERNST JACOBY (*Ber.*, 1908, 41, 2393—2398. Compare Abstr., 1906, i, 237).—Attempts to prepare carbethoxycarbimide from potassium cyanate and ethyl chlorocarbonate led to the formation of only small amounts of the desired product, which is difficult to separate from the ethyl carbonate formed simultaneously (compare Wilm, Abstr., 1878, 851; Wurtz and Henninger, Abstr., 1885, 968). Carbethoxycarbimide is extremely stable at high temperatures, and could not be converted into Wurtz and Henninger's polymeride by heating. When treated with concentrated sulphuric acid, it is hydrolysed, yielding carbon dioxide and urethane, whereas with water, carbon dioxide and carbonyldiurethane, $CO(NH\cdot CO_2Et)_2$, are formed. Carbethoxycarbimide reacts energetically with amines, forming ethyl allophanates, $NHR\cdot CO\cdot NH\cdot CO_2Et$, but with anthranilic acid, it yields carbon dioxide and the *derivative*, $CO_2Et\cdot NH\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot CO_2Et$, which decomposes at 225°, and has acid properties, forming a crystalline *potassium* salt.

With alcohols, phenols, and oximes, carbethoxycarbimide reacts normally, forming iminodicarboxylic esters, $CO_2R\cdot NH\cdot CO_2Et$, whilst with acetic anhydride, acetylurethane, $NHAc\cdot CO_2Et$, is formed, diacetylurethane, $NAc_2\cdot CO_2Et$, being probably the intermediate product. With phenol, carbethoxycarbimide forms a *product*, $C_{10}H_{11}O_4N$, which is obtained as a hygroscopic oil, b. p. 136—139°. *iso*Nitrosomethyl propyl ketone and carbethoxycarbimide form a *substance*, $C_9H_{14}O_5N_2$, crystallising in small needles, m. p. 44—46°.

The action of hydrogen cyanide on carbethoxycarbimide leads to the formation of a *product*, $CO_2Et\cdot NH\cdot CO\cdot N(CO_2Et)\cdot CO\cdot CN$ or



$CO_2Et\cdot N{<}\begin{matrix}CO\text{——}N\cdot CO_2Et\\ C(NH)\cdot CO\end{matrix}$, which is obtained as a white, crystalline powder, m. p. 125° (decomp.), has slight acid properties, and when dissolved in alkali and treated with carbon dioxide evolves hydrogen cyanide. G. Y.

Preparation of Soluble and Stable Additive Compounds of Thiocarbamide and Silver Salts. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 193661).—The double compounds of thiocarbamide and silver salts hitherto known, which contain one atom of silver combined with one to three molecules of thiocarbamide, are sparingly soluble and readily decomposed. It has now been found that soluble and stable additive compounds may be produced by combining the components in the proportion of 1 atom of silver to 5 molecules of the base. The *substance*, $5CH_4N_2S,AgCl$, is obtained by evaporating to dryness an aqueous solution of its components and crystallising the residue from alcohol. A similar product may be obtained from silver nitrate. G. T. M.

Action of Iodine on Certain Thiocyanates. PAUL PFEIFFER and M. TILGNER (*Zeitsch. anorg. Chem.*, 1908, **58**, 433—442).—The *compound*, $[CoPy_4(SCN)_2]2I_2$, prepared by boiling an alcoholic solution of tetrapyridinecobalt thiocyanate, $CoPy_4(SCN)_2$, and iodine for one to two hours, separates from the solution on cooling in black, lustrous crystals, which lose about 2 mols. of pyridine and almost all the iodine on heating to 100°. The corresponding *nickel* compound, $[NiPy_4(SCN)_2]2I_2$, prepared by an analogous method, also occurs in lustrous, black crystals, which decompose slowly in the air, and behave like the cobalt compound when heated at 100°. Both compounds are additive products of iodine and the corresponding salts. An isomeric form of tetrapyridinecobalt thiocyanate, described by Sand (Abstr., 1903, i, 467) as being formed by the action of iodine on the ordinary form of the salt, does not appear to exist.

When triethylenediaminecobalt thiocyanate, $[CoEn_3](SCN)_3$, is heated with iodine in alcoholic solution, the thiocyanate group is displaced by iodine, and from the solution the additive *compound*, $[CoEn_3]I_3,2I_2$, separates in lustrous, deep black needles. The same compound is obtained by the action of iodine on triethylene diamine-cobalt iodide, $[CoEn_3]I_3$; it is decomposed on boiling with dilute acids.

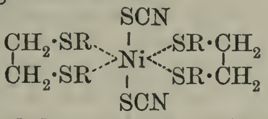
The *compound*, $[Cr(NH_3)_2(SCN)_4]NH_4I$, first obtained by Nordenskiöld (Abstr., 1893, i, 290), has been prepared, and the above formula confirmed. As the halogens appear invariably to unite as molecules, it is probable that the compound in question has the doubled formula $\{[Cr(NH_3)_2(SCN)_4]NH_4\}_2I_2$. G. S.

Halogen Compounds of Molybdenum and Tungsten. IV. Thiocyanates of Tervalent Molybdenum. ARTHUR ROSENHEIM and ABRAHAM GARFUNKEL (*Ber.*, 1908, **41**, 2386—2392. Compare Abstr., 1905, ii, 717; 1906, i, 603; 1907, i, 688).—A discussion of the constitution of the molybdenum salts described by Sand and his co-workers (Abstr., 1906, i, 487; this vol., i, 11, 397, 513). Maas and Sand's potassium salt, $[Mo(SCN)_6(OH_2)]K_3,4H_2O$, is considered not to contain water or hydroxyl of constitution, and to be identical with Chilesotti's salt, $K_3Mo(SCN)_6,4H_2O$ (Abstr., 1906, ii, 263, 365). When treated with thallium nitrate in aqueous solution, it forms an amorphous, light yellow *precipitate*, $Tl_2Mo(SCN)_6$. It is found that the molybdenum of these salts can be oxidised by ammoniacal silver nitrate and the equivalent of the molybdenum calculated from the amount of silver liberated. The results obtained are sufficiently in agreement with those required by a tervalent molybdenum atom.

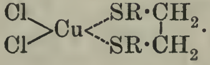
The metal-ammonium salts described by Sand and his co-workers must therefore be considered to be salts of the complex anion, $Mo(SCN)_6'''$. The zinc-ammonium salt on analysis gives figures agreeing with the formula $[Zn(NH_3)_4]_3[Mo(SCN)_6]_2$. Sand and Burger's pyridine salt, $6C_5H_5N,H_3Mo(SCN)_6$ (Abstr., 1905, i, 923; 1906, i, 487), loses $3C_5H_5N$ over sulphuric acid in a vacuum, yielding a dark red salt, $3C_5H_5N,H_3Mo(SCN)_6$; 3 mols of pyridine must therefore be pyridine of crystallisation. Sand and Burger's tetrapyridine salt is the dark red tripyridine salt crystallised with $3H_2O$.

G. Y.

Complex Compounds of Organic Disulphides. LEO A. TSCHUGAEFF (*Ber.*, 1908, 41, 2222—2226. Compare Abstr., 1906, i, 814, 984; 1907, i, 17, 392, 595, 830, 896; Werner, this vol., i, 440).—A survey of the previous work shows that the most stable complex metal compounds are those where penta-atomic rings are formed; the hexa-atomic rings are less stable, and there appears to be little or no tendency for other rings to be formed. Phillips (Abstr., 1901, i, 444) has shown that organic sulphides form double compounds with the salts of heavy metals, and the author has prepared and investigated the behaviour of disulphides of the general formula $R{\cdot}S{\cdot}[CH_2]_n{\cdot}S{\cdot}R'$. The monosulphides do not give or give very unstable complexes with nickel or cupric salts; on the other hand, the disulphides, where $n = 2$, give stable compounds with nickel thiocyanate and cupric chloride, where R = Me, Et, *iso*butyl, or *iso*amyl. In compounds where $n = 0, 1, 3$, or 5, no such complexes are formed. The only exception so far found is $Ph{\cdot}S{\cdot}[CH_2]_2{\cdot}S{\cdot}Ph$, which does not give a complex compound with copper chloride or nickel thiocyanate. On the basis of Werner's co-ordination theory, these compounds are assigned the following constitutions:



$$\begin{matrix} & \mathrm{SCN} & \\ & | & \\ \mathrm{CH_2{\cdot}SR} & & \mathrm{SR{\cdot}CH_2} \\ | & >\mathrm{Ni}< & | \\ \mathrm{CH_2{\cdot}SR} & & \mathrm{SR{\cdot}CH_2} \\ & | & \\ & \mathrm{SCN} & \end{matrix}$$



$$\begin{matrix} \mathrm{Cl} & & \mathrm{SR{\cdot}CH_2} \\ & >\mathrm{Cu}< & | \\ \mathrm{Cl} & & \mathrm{SR{\cdot}CH_2} \end{matrix}.$$

The *ethyl* compound, $Ni(SEt{\cdot}[CH_2]_2{\cdot}S{\cdot}Et)_2(SCN)_2$, prepared by shaking the disulphide with an aqueous solution of the nickel salt for a few minutes, forms blue needles from 80—90% alcohol, and is quickly decomposed by water into its components. It loses half of its disulphide at 100°, and does not melt at 210°. The *methyl*,

$$Ni(SMe{\cdot}[CH_2]_2{\cdot}SMe)_2(SCN)_2,$$

and iso*amyl*, $Ni(SC_5H_{11}{\cdot}[CH_2]_2{\cdot}SC_5H_{11})(SCN)_2$, derivatives are similar.

The copper derivatives are prepared in a similar way in the presence of hydrochloric acid. The *ethyl* derivative,

$$Cu(SEt{\cdot}[CH_2]_2{\cdot}SEt)Cl_2,$$

forms dark green, almost black, prismatic needles, m. p. 113°; the iso*butyl* compound is similar, m. p. 115°. They are more easily decomposed by water than the nickel compounds.

The diselenides appear to behave in a similar manner. W. R.

Cobalt Dioximines. III. New Complex Acid. LEO A. TSCHUGAEFF (*Ber.*, 1908, 41, 2226—2232).—One series of monobasic salts has been described, which contain the cation $(Co2aD_2H_2)$ (Abstr., 1906, i, 814), and another series (Abstr., 1907, i, 904) of the general type $(CoaXD_2H_2)$, which are non-ionisable. [$D = R{\cdot}C(\colon NO{\cdot}){\cdot}C(\colon NO{\cdot}){\cdot}R$, a = ammonia or amine, X = an acidic radicle.] In accordance with the co-ordination theory, a third series should be capable of existence in which the cobalt group would be the anion, and this type has now been obtained.

Sodium cobaltidinitrodimethylglyoximinate, $Na[Co(NO_2)_2D_2H_2]$, is obtained by digesting a 10% solution of sodium cobaltihexanitrite with excess of dimethylglyoxime until nitrous fumes cease to be evolved. After filtration, the salt crystallises out on evaporation :

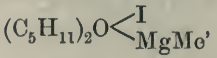
$$Na_3[Co(No_2)_6] + 2DH_2 = Na[Co(NO_2)_2D_2H_2] + 2NaNO_2 + 2HNO_2,$$

a reaction similar to the formation of the diamminochloride,

$$[Co2NH_3D_2H_2]Cl,$$

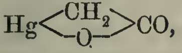
from the luteo-salt, $[Co6NH_3]Cl_3$. The other salts described are obtained from this by double decomposition ; the *ammonium* salt, $NH_4[Co(NO_2)_2D_2H_2],H_2O$, forms brownish-yellow needles ; the *ethylammonium*, $NH_3Et[Co(NO_2)_2D_2H_2],H_2O$, *diisobutylammonium*, $NH_2(C_4H_9)_2[Co(NO_2)_2D_2H_2]$, *potassium*, *rubidium*, and *caesium* salts have been prepared. The *acid*, $H[Co(NO_2)_2D_2H_2],H_2O$, separates from a 5—10% solution of the sodium salt on the addition of hydrochloric acid as microscopic, hexagonal plates. It reddens litmus and decomposes carbonates, and from determinations of the molecular conductivity of the acid and its alkali salts, it is calculated that the mobility of the anion $[Co(NO_2)_2D_2H_2] = 18{\cdot}0$ at 25°, and that the free acid is ionised to the extent of 88% at $\nu = 250$. The molecular conductivity of its aqueous solutions gradually decreases (thus $\nu = 250$, $\mu = 338{\cdot}3$, after forty hours $320{\cdot}0$), due to the liberation of nitrous acid. It is fairly stable in the solid state in the air, but in a closed vessel it quickly decomposes, due perhaps to catalytic action of the nitrous acid. It rapidly loses water and nitrous acid at 100—110°. When an aqueous solution is gently warmed, a dark brown, crystalline precipitate of *cobaltinitroaquodimethylglyoximine*, $[CoNO_2,H_2O,D_2H_2]$, is produced. It is a non-electrolyte ($\mu = 3{\cdot}0$, $\nu = 1000$), and the nitro group is firmly attached to the molecule.

Stable compounds containing the thiocyanate radicle instead of the nitro-group and less stable derivatives containing chlorine and iodine are under examination. W. R.

Crystalline Compound of Magnesium Methiodide and Amyl Ether. TH. ZEREWITINOFF (*Ber.*, 1908, 41, 2244—2245).—The compounds of ether and magnesium alkyl iodides hitherto obtained are not crystallisable (Grignard, Abstr., 1901, i, 679 ; Blaise, 1901, i, 317 ; Baeyer and Villiger, 1902, i, 355 ; Tschelinzeff, 1906, i, 241), but when paraffin is added to the product obtained after interaction of 78—80 c.c. of amyl ether, 6 grams of magnesium, and 35·5 grams of methyl iodide, and the mixture left for some days, large, transparent crystals of the *compound*,  $(C_5H_{11})_2O{<}\begin{smallmatrix}I\\ MgMe\end{smallmatrix}$, separate. They are unstable in the air.

W. R.

Synthesis of α-Hydroxymercuri-fatty Acids. I. Methyl Mercuridimalonate and its Product of Hydrolysis, Hydroxymercuriacetic Anhydride. WALTER SCHRAUTH and WALTER SCHOELLER (*Ber.*, 1908, 41, 2087—2094. Compare Fischer, this vol., i, 200).—The physiological importance of the α-amino-acids led to the idea of substituting different basic radicles for the amino-group and so forming other α-basic acids, which might be expected to have interesting physiological actions. The present paper is a study of the introduction of the hydroxymercuri-group, ·Hg·OH, into the α-position in fatty acids.

Methyl mercuridimalonate, $Hg[CH(CO_2Me)_2]_2$, is formed when methyl malonate suspended in water is gently heated and shaken with mercuric oxide; it crystallises from chloroform-ether in colourless plates, m. p. 127° (corr.), is readily soluble in organic solvents, is decomposed by halogens, forming the mercuric haloids, and yields mercuric sulphide when treated with ammonium sulphide. When shaken with *N*-sodium hydroxide, the mercuri-ester yields *hydroxymercuriacetic anhydride*,  $Hg{<}\genfrac{}{}{0pt}{}{CH_2}{O}{>}CO$, which is formed also by the action of mercuric oxide on sodium malonate; it is obtained as a hard mass, which becomes brown at 200°, decomp. 250° (detonates). The *sodium* salt forms needles, is alkaline in aqueous solution, does not coagulate albumin, and does not yield mercury in contact with copper, but forms mercuric sulphide, as does also the anhydride, when treated with ammonium sulphide, and on electrolysis in alkaline solution deposits sodium amalgam at the cathode; this reaction is not reversible, as a mercury anode is not dissolved, and hence the mercury in sodium mercuriacetate is not ionised. The *copper* salt, $Hg_2C_4H_6O_6Cu$, was analysed; the *calcium*, *silver*, *lead*, and *mercuric* salts are white powders. The sodium and calcium salts act as antiseptics towards yeast; at the same time, the poisonous action of the mercury is much diminished. With hydrochloric acid, the anhydride forms mercuric chloride, but it is not attacked by cold dilute sulphuric acid, and when dissolved in nitric acid (D 1·2) and further diluted with water or alcohol, yields a white *precipitate*, which is probably the nitrate of mercuriacetic acid. Treatment of the anhydride with 10% ammonia leads to the formation of a yellowish-white, granular precipitate of varying and complicated composition.

When treated with anhydrous formic acid, the anhydride is converted into the *formate* of dihydroxymercuriacetylhydroxymercuriacetic acid, $CHO{\cdot}O{\cdot}Hg{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}Hg{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}Hg{\cdot}CH_2{\cdot}CO_2H$, which is obtained as a colourless, crystalline substance, decomposing on exposure to light.

Attempts to isolate mercuridimalonic acid or mercuridiacetic acid as intermediate products in the hydrolysis of methyl mercuridimalonate were unsuccessful. G. Y.

Ethyl*cyclo*butane. NICOLAI ZELINSKY and J. GUTT (*Ber.*, 1908, 41, 2431—2434).—The scanty knowledge of *cyclo*butane hydrocarbons has induced the authors to commence an investigation of such compounds. The reaction between magnesium methyl iodide and *cyclo*butanecarboxylamide leads to the formation of methyl *cyclo*butyl ketone, b. p. 136—136·5°/750 mm., $n_D^{19\cdot3}$ 1·4322, D_4^{10} 0·9112, D_4^{20} 0·9020 (compare Perkin, Trans., 1892, 61, 48), the *semicarbazone* of which has m. p. 148—149°. By reduction with sodium in moist ether at 0°, the ketone yields methyl*cyclo*butylcarbinol, b. p. 144°/752 mm., $n^{18\cdot8}$ 1·14451, D_4^{10} 0·9075, of which the *phenylurethane* has m. p. 87·5—88°. When treated with hydriodic acid, D 1·96, the carbinol yielded an oily iodide which, without being isolated, was reduced by glacial acetic acid and zinc dust, forming a saturated *hydrocarbon*, C_6H_{12}, b.p. 72·2—72·5° (corr.), $n^{19\cdot5}$ 1·4080, D_4^{20} 0·7450; this is oxidised by nitric acid to succinic acid. The hydrocarbon is therefore ethyl*cyclo*butane.

The authors are investigating methyl*cyclo*pentane, which closely resembles the preceding isomeric hydrocarbon, and is oxidised by nitric acid to succinic acid and not to glutaric acid, as would be expected. C. S.

Occurrence of Nononaphthene in Coal Tar. FELIX B. AHRENS and LEO VON MOŹDŹEŃSKI (*Zeitsch. angew. Chem.*, 1908, 21, 1411—1414).—Xylene obtained from coal tar was found on nitration to yield an oil (b. p. 137—139°, D^{15} 0·7662) which had escaped nitration and proved on analysis to be *nononaphthene*, C_9H_{18}. Ten c.c. of this oil heated for eight hours at 125—130° with 50 c.c. of nitric acid, D 1·075, yielded on fractionation an oil, b. p. 125—135°/40 mm., which by means of alcoholic sodium hydroxide was shown to consist of a mixture of tertiary and secondary nitro-derivatives. The *secondary* nitro-derivative, $C_9H_{17}\cdot NO_2$, is a colourless oil which turns yellow; it has a characteristic pungent odour, and has b. p. 115—120°/15 mm., 220—224°/760 (decomp.), D^{20} 0·9778, and n_D^{20} 1·451; on treatment with bromine it yields an oil containing 31·74% of bromine. The *tertiary* nitro-derivative, $C_9H_{17}\cdot NO_2$, b. p. 102—105°/12 mm., 217—225°/760 (decomp.), D^{20} 0·9771, n_D^{20} 1·449, is a colourless oil which also turns yellow. The *tertiary* nitro-derivative when reduced by means of hydrochloric acid and tin foil yielded a mixture of amines which were separated by conversion into their *picrates*, one of which, *A*, was soluble in benzene, the other, *B*, being insoluble in benzene, but soluble in water. The *picrate A* crystallises in rhombic leaflets, m. p. 176—177°; when decomposed with potassium hydroxide and distilled with steam it yields an *amine*, $C_9H_{17}\cdot NH_2$, b. p. 175—176°/760 mm., D^{15} 0·8205, n_D^{21} 1·447; the *hydrochloride*, $C_9H_{17}\cdot NH_2,HCl$, m. p. 155° (approx.); the *oxalate*, $C_{20}H_{40}O_4N_2$, white scales, darkens at 270° and decomposes without melting; the *platinichloride* and *aurichloride* are oils which gradually solidify, but were not analysed. The *picrate B*, which separates from water in long crystals, m. p. 187—188°, yields an *amine*, $C_9H_{17}\cdot NH_2$, b. p. 172—173°/773 mm., D^{20} 0·8500, n_D 1·448, which yields a *hydrochloride*, glistening crystals from alcohol, m. p. 184—185°, an *oxalate*, $C_{20}H_{40}O_4N_2$, white, amorphous mass, which decomposes without melting at 265°, a *platinichloride*, $(C_9H_{19}N)_2,H_2PtCl_6$, orange-yellow, envelope-shaped crystals, decomp. 290°, and an *aurichloride*, which crystallises like the platinichloride, m. p. 193—194° (decomp.).

The *secondary* amine, obtained by the reduction of the secondary nitro-derivative, has b. p. 175—177°/748 mm., D^{20} 0·8314, and n_D^{20} 1·445. Its *picrate* crystallises in four-sided plates, m. p. 173—174°, its *hydrochloride* is a liquid; its *platinichloride* forms glistening, yellow plates from water, decomp. 290°; the *aurichloride* is an amorphous, sticky substance; the *oxalate* forms white, glistening scales, decomp. 265°.

On oxidation with nitric acid, D 1·075, nononaphthene is converted into succinic acid; oxidation with nitric acid, D 1·5, converts it into butyric acid.

When treated with moist chlorine at 30° in diffused daylight, nononaphthene yields a monochloro-derivative, which is a colourless liquid with a pungent odour, b. p. 103—104°/40 mm., D^{20} 0·9229.

Bromine in the presence of aluminium bromide or finely-divided iron converts nononaphthene into tribromo-ψ-cumene, m. p. 234°. P. H.

Isomeric Dihydrobenzenes and Optically Active Dihydrotoluene. Nicolai D. Zelinsky and A. Gorsky (*Ber.*, 1908, **41**, 2479—2487).—An investigation on $\Delta^{1:3}$- and $\Delta^{1:4}$-*cyclo*hexadienes and on 1-methyl-$\Delta^{2:4}$-*cyclo*hexadiene, carried out chiefly with the object of ascertaining the effect of ethylene linkings on the optical properties of compounds.

The conclusions of Markownikoff (Abstr., 1899, i, 22) and Harries and Antoni (Abstr., 1903, i, 613) are shown to be incorrect. The tetrabromide, m. p. 188°, is derived from $\Delta^{1:4}$-*cyclo*hexadiene, whilst the tetrabromide obtained from $\Delta^{1:3}$-*cyclo*hexadiene has m. p. 140—141° (compare Crossley, Trans., 1903, **83**, 505).

Although $\Delta^{1:3}$-*cyclo*hexadiene and 1-methyl-$\Delta^{2:4}$-*cyclo*hexadiene contain contiguous double linkings, they do not follow Brühl's rule (Trans., 1907, **91**, 115). It is, however, not impossible that these compounds may have a dicyclic structure, since they do not readily form tetrabromo-derivatives, and are not readily oxidised.

$\Delta^{1:4}$-*cyclo*Hexadiene has b. p. 85·5° (corr.), D_4^{20} 0·8471, D_4^{15} 0·8519, n_D^{20} 1·4729, mol. ref. 26·50 (compare von Baeyer, Abstr., 1892, 1074; Brühl, Abstr., 1894, i, 366). It readily forms a tetrabromide, m. p. 188° (corr.); the *dibromide*, $C_6H_8Br_2$, has m. p. 95°, b. p. about 105°/15 mm.

$\Delta^{1:3}$-*cyclo*Hexadiene has b. p. 80·5° (corr.), D_4^{15} 0·8423, D_4^{20} 0·8376, n_D^{20} 1·4700, mol. ref. 26·66. It only combines readily with 1 mol. of bromine, forming a dibromide, m. p. 102—104, b. p. about 105°/14 mm. (compare Crossley, *loc. cit.*). A small quantity of the *tetrabromide*, $C_6H_8Br_4$, is obtained by acting on the hydrocarbon with bromine in light petroleum; it crystallises in prisms, m. p. 140—141° (corr.). The tetrabromide is not formed by acting on a solution of the dibromide with bromine in chloroform. $\Delta^{1:3}$-*cyclo*Hexadiene when shaken with nitric acid (1·4) becomes violet, whilst $\Delta^{1:4}$-*cyclo*hexadiene when similarly treated undergoes violent oxidation.

1-*Methyl*-$\Delta^{2:4}$-cyclo*hexadiene*, C_7H_{10}, is obtained by the action of quinoline on the dibromide of 1-methyl-Δ^{3}-*cyclo*hexene; it is a colourless liquid, b. p. 105·5—106° (corr.), D_4^{15} 0·8324, D_4^{20} 0·8274, n_D^{20} 1·4680, $[\alpha]_D$ 36·42. It is also obtained in small quantities by the action of an alcoholic solution of potassium hydroxide on the dibromide, when it has α_D 57·48° (100 mm. tube). The principal product is, however, *ethoxymethyl*cyclo*hexene*, $C_9H_{16}O$; it is a colourless liquid, b. p. 169°/750 mm., D_4^{20} 0·8762, D_4^{22} 0·8746, n_D^{22} 1·4480, mol. ref. 42·72, α_D 18·56° (100 mm. tube).

1-Methyl-$\Delta^{2:4}$-*cyclo*hexadiene becomes violet-blue when shaken with nitric acid (1·4); it combines with 1 mol. of bromine, yielding a *dibromide*, $C_7H_{12}Br_2$, b. p. 107—108°/15 mm., α_D 33·2° (100 mm. tube); a tetrabromide could not be obtained. W. H. G.

Lecture Experiments on the Preparation of Hydrocarbons. James F. Spencer (*Ber.*, 1908, **41**, 2302—2303).—The author gives instructions for the preparation of benzene and naphthalene by the action of magnesium on the corresponding halogen derivative as already described (Spencer and Stokes, Trans., 1908, **93**, 68). Pentane or *iso*pentane is prepared by heating amyl or *iso*amyl iodide respectively with magnesium and adding water to the product. J. C. C.

Derivatives of 2-Iodo-4-nitrotoluene with Polyvalent Iodine. Conrad Willgerodt and B. R. Kok (*Ber.*, 1908, **41**, 2077—2083).—*4-Nitro-o-toluidine hydrochloride*, $C_7H_8O_2N_2,HCl$, forms white needles, blackens at 200°, m. p. 230° (decomp.).

2-Iodo-4-nitrotoluene crystallises in rhombic plates, m. p. 58° (51°: Reverdin, Abstr., 1898, i, 180), and when treated with chlorine in chloroform solution is converted into the *iodochloride*, $NO_2\cdot C_6H_3Me\cdot ICl_2$, which crystallises in sulphur-yellow prisms, decomp. 83°. The action of sodium carbonate and sodium hydroxide on this leads to the formation of 2-*iodoso*-4-*nitrotoluene*, $NO_2\cdot C_6H_3Me\cdot IO$, which is obtained as an insoluble, yellowish-white powder, and explodes at 180—181°, having first changed into a mixture of the iodoxy- and iodo-compounds. 2-*Iodoxy*-4-*nitrotoluene*, $NO_2\cdot C_6H_3Me\cdot IO_2$, formed by the action of hypochlorous acid on the iodoso-compound, is obtained as a white, flocculent precipitate, which explodes at 204°.

The following iodonium salts, $R=(NO_2\cdot C_6H_3Me)_2I$, were prepared from a mixture of the iodoso- and iodoxy-compounds.

RCl: white needles, m. p. about 140°; RBr: decomp. 145°; RI: yellow needles, decomp. 113°; RNO_3: white needles, m. p. 147°; $RHSO_4$: white needles, m. p. 165°; $R_2Cr_2O_7$: orange-yellow, amorphous precipitate, explodes 128°; R_2PtCl_6: yellow leaflets, decomp. 180°.

Phenyl-4-*nitro*-2-*tolyliodonium hydroxide*, $NO_2\cdot C_6H_3Me\cdot IPh\cdot OH$, prepared by the action of silver oxide and water on a mixture of 2-iodoxy-4-nitrotoluene and iodosobenzene, is a strongly alkaline base. The following salts, $R'=NO_2\cdot C_6H_3Me\cdot IPh\cdot$, are described.

R'Cl: white needles, m. p. 183°; R'Br: yellow, flocculent precipitate, m. p. 165°; R'I: yellow needles, decomp. 131°; $R'I_3$: dark brown prisms, m. p. 50°; $R'NO_3$: white prisms, m. p. 167° (decomp.); $R'HSO_4$: white prisms, m. p. 142°; $R'_2Cr_2O_7$: yellow powder, m. p. 137—138° (explodes); $(R'Cl)_2HgCl_2$: white needles, m. p. 157° (decomp.); R'_2PtCl_6: yellowish-red prisms, m. p. 175° (decomp.).

4-*Nitro*-2-*tolyl*-o-*tolyliodonium hydroxide* is prepared in the usual manner from a mixture of 2-iodoxy-4-nitrotoluene and 2-iodosotoluene. The following salts, $R = NO_2 \cdot C_6H_3Me \cdot I(C_7H_7)$, are described.

RCl: white needles, m. p. 170°; RBr: needles, m. p. 151°; RI: decomp. 116°; $R_2Cr_2O_7$: explodes 136°; R_2PtCl_6: golden leaflets, m. p. 158°; $(RCl)_2HgCl_2$: needles, m. p. 168°. G. Y.

New Catalytic Effect of Aluminium Chloride. Eyvind Bœdtker (*Bull. Soc. chim.*, 1908, [iv], 3, 726—729.—It is shown that when nitro-compounds are employed in the Friedel-Crafts reaction, the nitro-group is eliminated and that through its agency the condensation product formed is in part oxidised. In certain cases it is possible to nitrate compounds by using nitrates in the Friedel-Crafts reaction.

Trichloronitromethane reacts with benzene in presence of aluminium chloride to form triphenylmethane and some triphenylcarbinol, the latter being formed by oxidation of the hydrocarbon by the eliminated NO_2 group.

Ethyl nitrate reacts with benzene in presence of aluminium chloride to form nitrobenzene, the other possible products of the reaction, namely, ethyl chloride, ethylbenzene and nitroethylbenzene, being formed, if at all, only in minute quantity. With toluene the principal product is the *o*-nitro-compound, with small quantities of the para-isomeride. With benzaldehyde a vigorous reaction, apparently involving the −CHO group, ensues, and *o*-nitrobenzaldehyde is not obtained. In these nitration reactions the hydrocarbon should be used in excess, and as water is always formed, considerable quantities of aluminium chloride are required. With benzene and amyl nitrite under similar conditions, some nitrosobenzene is formed, but the quantity is too small to be isolated. T. A. H.

Naphthalenesulphonates of Cerium. Hugo Erdmann and Theodor Nieszytka (*Annalen*, 1908, **361**, 166—189. Compare Abstr., 1893, i, 651).—The cerium salts described were prepared by the action of the naphthalenesulphonic acids on cerium carbonate in aqueous solution and evaporation to crystallisation. The solubilities of the salts in water and methyl and ethyl alcohol are tabulated; the solubility increases with the number of sulphonic groups, but is small if a β-substituting group is present. The solubilities of cerium hydrogen naphthalene-β-sulphonate and the basic 1 : 5-disulphonate could not be determined, as the salts are unstable. The small solubility of cerium anthraquinonesulphonate is remarkable; the complete insolubility of cerium 8-hydroxynaphthalene-1-sulphonate and its characteristic colour allow of its utilisation in analysis.

Cerium naphthalene-α-sulphonate, $(C_{10}H_7O_3S)_3Ce$, crystallises in nacreous leaflets, has an acid reaction, and forms precipitates with ammonia, potassium hydroxide, potassium hydroxide and hydrogen peroxide, ammonium oxalate, and barium hydroxide or chloride in aqueous solution, or with benzidine in acetic acid solution, and a bluish-red precipitate with ammonium 1 : 8-hydroxynaphthalenesulphonate; these precipitations in aqueous solution are retarded by the presence of hydroxy-acids of the fatty series.

Cerium naphthalene-β-sulphonate, $(C_{10}H_7O_3S)_3Ce,H_2O$, forms large, white leaflets, and gives similar precipitates to those of the α-salt.

Cerium naphthalene-1 : 5-*disulphonate*, $[C_{10}H_6(SO_3)_2]_3Ce_2,\frac{1}{2}H_2O$, loses $\frac{1}{2}H_2O$ at 180°, and can be recrystallised without decomposing.

Cerium naphthalene-2 : 7-*disulphonate*, $[C_{10}H_6(SO_3)_2]_3Ce_2,3H_2O$, loses $3H_2O$ on prolonged exposure to air, more quickly in a desiccator, has a strong acid reaction, and with benzidine in hot acetic acid solution forms the benzidine salt.

Cerium naphthalene-2 : 6-*disulphonate*, $[C_{10}H_6(SO_3)_2]_3Ce_2,H_2O$, loses $\frac{1}{2}H_2O$ at 135°, but H_2O at the ordinary temperature.

Cerium naphthalene-1 : 6-*disulphonate*, $[C_{10}H_6(SO_3)_2]_3Ce_2,4H_2O$, loses $4H_2O$ in a desiccator.

Cerium naphthalene-1 : 3 : 5-*trisulphonate*, $C_{10}H_5(SO_3)_3Ce,\frac{3}{4}H_2O$, crystallises in white scales, loses its water of crystallisation in a desiccator, has an acid reaction, is decomposed slowly by hydrogen peroxide, and forms a precipitate with benzidine in aqueous hydrochloric acid solution.

Cerium naphthalene-1 : 3 : 6-*trisulphonate* ($\frac{3}{4}H_2O$) forms yellow scales and loses water slowly in a desiccator.

Cerium naphthalene-1 : 3 : 7-*trisulphonate* ($1\frac{1}{4}H_2O$) loses its water of crystallisation slowly on exposure to air.

Cerium 1-*naphthol*-8-*sulphonate*, $(C_{10}H_7SO_4)_3Ce,3H_2O$, formed from the ammonium sulphonate, forms a bluish-brown, amorphous precipitate, loses $3H_2O$ at 110°, has an acid reaction, is unstable, and dissolves in acids, forming bluish-red solutions. The action of the free naphtholsulphonic acid on cerium carbonate leads to the formation of a blue *basic salt*, $(C_{10}H_6SO_4)_3Ce_2$, which also dissolves in acids, forming bluish-red solutions.

Cerium chromotropate, $[C_{10}H_4(OH)_2(SO_3)_2]_3Ce_2,4H_2O$, formed from 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid, is salted out of its solution; it forms a greyish-brown, microcrystalline mass, loses $4H_2O$ at 195°, has an acid reaction, and in concentrated solution commences only after some weeks to change into a basic salt, the edges of the solution becoming blue.

Cerium anthraquinonesulphonate, $(C_{14}H_7O_2\cdot SO_3)_3Ce,3H_2O$, forms green leaflets, loses $3H_2O$ at 187—195°, is very stable, has a strong acid reaction, and gives insoluble precipitates with benzidine, aniline, and toluidine. G. Y.

[Naphthalenesulphonates and Malonates of the] Rare Earths. Hugo Erdmann and Fritz Wirth (*Annalen*, 1908, 361, 190—217).—See this vol., ii, 694.

The Stilbene Series. Fritz Ullmann and Meinrad Gschwind (*Ber.*, 1908, 41, 2291—2297).—It is well known that a halogen atom in the benzene nucleus can readily be replaced by other substituents provided it is accompanied by a nitro-group in the ortho- or para-position; moreover, when the number of nitro-groups in the molecule is increased, the reactivity increases, and this is not diminished when, in the dinitro-derivatives, one nitro-group is replaced by a sulphonic, carboxylic, or aldehydic group. The authors have accordingly examined the behaviour of negatively-substituted toluene derivatives and find that, when one of the nitro-groups in 2 : 4-dinitrotoluene is replaced by a carboxylic, sulphonic, or cyanogen group, the resulting compound condenses with benzaldehyde in presence of piperidine with the production of the corresponding stilbene derivatives just as 2 : 4-dinitrotoluene itself, under similar conditions, yields dinitrostilbene (Thiele and Escales, Abstr., 1901, i, 689). Further, 2 : 4 : 6-trinitrotoluene condenses with benzaldehyde more readily and at a lower temperature than do the disubstituted derivatives.

2-*Nitrostilbene*-4-*sulphonamide*, $CHPh\colon CH\cdot C_6H_3(NO_2)\cdot SO_2\cdot NH_2$, prepared by condensing *o*-nitrotoluene-*p*-sulphonamide (Reverdin and Crépieux, Abstr., 1901, i, 685), forms yellow needles, m. p. 184°. It is readily reduced by stannous chloride and hydrochloric acid to 2-*amino-stilbene*-4-*sulphonamide*, which crystallises from alcohol in colourless leaflets, m. p. 206—207°. Its solutions in glacial acetic acid or alcohol exhibit a blue fluorescence. The *acetyl* derivative forms stellate aggregates of white needles, m. p. 205°. 4-Nitrotoluene-2-sulphonamide does not condense well with benzaldehyde, but 4-*nitrotoluene*-2-*sulphonanilide*, m. p. 148°, prepared by condensing 4-nitrotoluene-2-sulphonyl chloride with aniline, readily condenses, forming 4-*nitrostilbene*-2-*sulphonanilide*, which crystallises from glacial acetic acid in yellow needles, m. p. 206°. Similarly, *o*-nitro-*p*-toluonitrile furnishes 2-*nitro*-4-*cyanostilbene*, $CHPh\colon CH\cdot C_6H_3(NO_2)\cdot CN$, yellow needles, m. p. 170°, the *dibromo*-derivative, $C_{15}H_{10}O_2N_2Br_2$, of which forms colourless needles, m. p. 155—160° (decomp.). 2-*Amino*-4-*cyanostilbene* forms pale yellow crystals, m. p. 123°; its solutions in benzene, acetic acid, and ether show a blue fluorescence, whilst that in alcohol is bluish-green. The *acetyl* derivative, colourless needles, has m. p. 220°. 2-*Nitrostilbene*-4-*carboxylic acid*,

$$CHPh\colon CH\cdot C_6H_3(NO_2)\cdot CO_2H,$$

prepared by hydrolysis of the nitrile, crystallises from glacial acetic acid in small, yellow needles, m. p. 236°. It is also formed when ethyl 2-nitrotoluene-4-carboxylate is condensed with benzaldehyde, the ester being hydrolysed in the reaction.

2-*Aminostilbene*-4-*carboxylic acid*, prepared by reducing the nitro-compound, is a pale yellow, crystalline powder, m. p. 197—198°. Its solutions show a bluish-green fluorescence.

4-*Nitro*-2-*cyanostilbene*, prepared from *p*-nitro-*o*-toluonitrile, separates from glacial acetic acid in small, yellow needles, m. p. 142°. 2 : 4 : 6-*Trinitrostilbene*, obtained from 2 : 4 : 6-trinitrotoluene, crystallises from glacial acetic acid in yellow, glistening needles, m. p. 156°. 2 : 4 : 6 : 4′-*Tetranitrostilbene*, prepared by condensing 2 : 4 : 6-trinitrotoluene and *p*-nitrobenzaldehyde, forms yellow, glistening needles, m. p. 196°. J. C. C.

Colourless and Coloured Triphenylmethyl. JULIUS SCHMIDLIN (*Ber.*, 1908, **41**, 2471—2479. Compare this vol., i, 150; Gomberg, Abstr., 1907, i, 504; Tschitschibabin, Abstr., 1907, i, 1022).—A freshly-prepared solution of pure triphenylmethyl in benzene remains colourless for a few seconds and then gradually becomes orange-yellow. The colour of the solution disappears, however, when the latter is shaken with air, reappearing again after a time, and again disappearing when agitated with air, until finally the solution remains permanently colourless. The conclusion is therefore drawn that the yellow solutions of triphenylmethyl contain both a coloured and a colourless form of triphenylmethyl. The two forms are convertible one into the other, and are present in solutions and in the solid substance in a definite state of equilibrium, which depends both on the nature of the solvent and on the temperature.

The disappearance and reappearance of the colour of solutions of triphenylmethyl is due to the fact that the coloured variety oxidises far more rapidly than the colourless form. On shaking an ethereal solution of triphenylmethyl with air, the yellow form is oxidised, yielding the peroxide, which being insoluble in ether may be filtered off; the colourless filtrate quickly becomes yellow, and on shaking yields a further quantity of peroxide. It is found from the amount of peroxide formed that an ethereal solution of triphenylmethyl contains roughly ten times as much of the colourless form as of the coloured form. The latter substance must consequently have an exceedingly intense colour.

The yellow form also absorbs iodine far more rapidly than the colourless form. When a quantity of iodine, slightly more than sufficient to combine with the triphenylmethyl present in the yellow form, is added to a solution of triphenylmethyl in chloroform, a reddish-brown solution is obtained. The colour of the solution slowly changes, and when a sufficient quantity of the yellow variety has been formed, the solution has the pure yellow colour of triphenylmethyl iodide.

The state of equilibrium, triphenylmethyl (colourless) $\rightleftharpoons$ triphenylmethyl (coloured), is displaced towards the left by lowering the temperature. A solution of triphenylmethyl in chloroform, which is orange-yellow at 15°, becomes quite colourless at $-63°$; the change in the colour intensity of a solution of triphenylmethyl iodide when similarly treated is barely perceptible. W. H. G.

p-**Benzhydryltetraphenylmethane.** Alexei E. Tschitschibabin (*Ber.*, 1908, **41**, 2421—2428).—In connexion with the constitution of triphenylmethyl, hexaphenylethane, $CPh_3 \cdot CPh_3$, is a substance of great importance. Both Ullmann and Borsum (Abstr., 1902, i, 755) and Gomberg (Abstr., 1903, i, 244) thought they had obtained this hydrocarbon, the former by the action of zinc on triphenylchloromethane, and the latter by the polymerisation of triphenylmethyl. The behaviour of the hydrocarbon with bromine led the author to the view that it was *p*-benzhydryltetraphenylmethane, $CPh_3 \cdot C_6H_4 \cdot CHPh_2$ (Abstr., 1905, i, 125). He has now succeeded in definitely establishing this constitution. The stages of the proof are the following: Benzoyl chloride and triphenylmethane in the presence of aluminium chloride yield the well-known *p*-benzoyltriphenylmethane, the reaction of which with magnesium phenyl bromide leads to the formation of *p*-benzhydryltriphenylcarbinol, $CHPh_2 \cdot C_6H_4 \cdot CPh_2 \cdot OH$; the condensation of the carbinol or its chloride and aniline hydrochloride in boiling glacial acetic acid results in the production of amino-*p*-benzhydryltetraphenylmethane hydrochloride, $CHPh_2·C_6H_4·CPh_2·C_6H_4·NH_2,HCl$, and from the sulphate by the replacement of the amino-group by hydrogen by the diazo-reaction, Ullmann and Borsum's "hexaphenylethane" is obtained, $CHPh_2·C_6H_4·CPh_3$.

A second modification of *p*-benzoyltriphenylmethane, m. p. 150°, is obtained by crystallisation from glacial acetic acid. p-*Benzhydryltriphenylcarbinol* separates from alcohol in colourless crystals, m. p. 135—137°, but the crystals from other solvents obstinately retain benzene of crystallisation. The purification of the crude carbinol is therefore best effected through the *ethyl ether*,

$$CHPh_2·C_6H_4·CPh_2·OEt,$$

m. p. 186°, which is obtained in nearly theoretical yield by adding a drop of acetyl chloride to the alcoholic solution of the carbinol. The *chloride* has m. p. 142°, becoming orange-coloured; the *bromide* melts at 140° to an orange liquid. *Amino*-p-*benzhydryltetraphenylmethane*, m. p. 195—198° (decomp.), is best purified through the *hydrogen sulphate*, m. p. 194—196° (decomp.). The *diazo-sulphate*, obtained by means of amyl nitrite in glacial acetic acid, decomposes at 120°, and by treatment with boiling alcohol yields *p*-benzhydryltetraphenylmethane and the *ethyl ether* of the phenol derived from the diazo-salt, m. p. 184°. C. S.

Preparation of Ethyl Phenylglycinate. GEORGES IMBERT UND CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 194884).—Ethyl phenylglycinate, $NHPh·CH_2·CO_2Et$, may be readily prepared by heating to boiling a mixture of ethyl chloroacetate, aniline, water, and calcium carbonate; carbon dioxide is evolved, and the fused product is separated from the calcium chloride solution. G. T. M.

Action of Cyanogen Bromide and of Bromine on Aromatic Derivatives of Aminoacetonitrile. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2100—2113).—In order to ascertain if the action of cyanogen bromide on arylaminoacetonitriles is similar to that observed in the case of the alkylamino-derivatives (Abstr., 1907, i, 899), the author has selected the cases of methyl- and ethyl-anilinoacetonitrile, and finds that the interaction is quite different, the chief product in each case being the corresponding *p*-bromophenyl derivative. As by-products were obtained compounds of the formulæ $C_{18}H_{18}N_4$ and $C_{20}H_{22}N_4$ respectively, the constitution of which has not yet been elucidated.

p-*Bromophenylmethylaminoacetonitrile*, $C_6H_4Br·NMe·CH_2·CN$, prepared by heating methylanilinoacetonitrile and cyanogen bromide in a closed vessel for five hours on the water-bath, has b. p. 205—206°/22 mm., m. p. 40°. On warming with 25% sulphuric acid, *p*-bromodimethylaniline is formed. The *compound*, $C_{18}H_{18}N_4$, crystallises from alcohol in colourless, glistening leaflets, m. p. 103°. It is hydrolysed by hydrochloric or sulphuric acid (25—38%) to an *amino-acid*, obtained as a dark viscous oil, and, on one occasion only, a substance was isolated which was probably trimethyldiaminodiphenylmethane.

s-ω-*Dicyanotetramethylbenzidine*, $C_{12}H_8(NMe·CH_2·CN)_2$, prepared from *s*-dimethylbenzidine and iodoacetonitrile, forms glistening, brown leaflets, m. p. 203°. *ω-Dicyanodiphenyldimethylethylenediamine*, $C_2H_4(NPh{\cdot}CH_2{\cdot}CN)_2$, obtained from diphenylethylenediamine and bromo- or iodo-acetonitrile, crystallises from alcohol in white leaflets, m. p. 131°. Neither this nor the foregoing substance is identical with the compound, m. p. 103°.

p-*Bromophenylethylaminoacetonitrile*, $C_6H_4Br{\cdot}NEt{\cdot}CH_2{\cdot}CN$, prepared from ethylanilinoacetonitrile and cyanogen bromide, has b. p. 195°/8 mm. and m. p. 56°. On hydrolysis it yields *p*-bromomethylethylaniline, of which the *platinichloride* is a red oil, and the *methiodide* a hygroscopic solid. *Methyl*-p-*toluidinoacetonitrile*,

$$C_6H_4Me{\cdot}NMe{\cdot}CH_2{\cdot}CN,$$

prepared from methyl-*p*-toluidine by Knoevenagel's method (Abstr., 1904, i, 989), has b. p 156—157°/9 mm. and m. p. 57°; it is not acted on by cyanogen bromide. (A convenient method of preparing methyl-*p*-toluidine consists in demethylating dimethyltoluidine with cyanogen bromide. p-*Tolylmethylcyanamide*, $C_6H_4Me{\cdot}NMe{\cdot}CN$, b. p. 147°/9 mm., m. p. 45°, is formed together with *p*-tolyltrimethylammonium bromide, which on dry distillation gives methyl bromide and dimethyltoluidine, and the cyanamide is converted into methyl-*p*-toluidine by boiling with 30% sulphuric acid for one hour. *Benzoylmethyl*-p-*toluidine*, $C_6H_4Me{\cdot}NMeBz$, has b. p. 198—199°/9 mm. and m. p. 53°.) *a*-Methylanilinopropionitrile, prepared by Sachs and Kraft's method (Abstr., 1903, i, 335), with the difference that the components are heated with alcohol for six instead of two hours, is also unacted on by cyanogen bromide.

When methylanilinoacetonitrile is treated with bromine in chloroform solution, a white substance separates, which is probably *p*-bromophenylmethylaminoacetonitrile hydrobromide, and this, on addition of water, gives the nitrile. Similarly, methyl-*p*-toluidinoacetonitrile furnishes m-*bromo*-p-*tolylmethylaminoacetonitrile*,

$$C_6H_3BrMe{\cdot}NMe{\cdot}CH_2{\cdot}CN,$$

strongly refracting crystals, b. p. 161—165°/10 mm., m. p. 47°, which on hydrolysis yields *m*-bromodimethyl-*p*-toluidine. The latter is most conveniently prepared by brominating dimethyltoluidine, and has b. p. 243—244°/752 mm. (Pesci, *Gazzetta*, 1898, **28**, i, 101, gives b. p. 237—238°/744 mm.).

The *platinichloride* forms reddish-yellow crystals, m. p. 212° (decomp.); the *picrate* has m. p. 115°. *Dimethyl*-p-*toluidine picrate* has m. p. 130°. J. C. C.

Preparation of Aromatic *o*-Nitroamino-derivatives. Fritz Ullmann (D.R.-P. 194951).—By heating the arylsulphonyl derivatives of *o*-nitrophenol and its analogues with a primary or secondary amine, the group $O{\cdot}SO_2R$ is replaced by an amino-residue and a secondary or tertiary amine is produced.

o-Nitrodiphenylamine is obtained by heating a mixture of aniline, *o*-nitrophenyl *p*-toluenesulphonate, and anhydrous sodium acetate. 2 : 4-Dinitrodimethylaniline is produced from 3 : 4-dinitrophenyl benzenesulphonate and dimethylamine.

2 : 4-Dinitrodiphenylamine-2-carboxylic acid can be thus prepared from 2 : 4-dinitrophenyl *p*-toluenesulphonate and anthranilic acid.

3 : 5-*Dinitro-4-benzylaminotoluene*, $C_6H_2Me(NO_2)_2 \cdot NH \cdot CH_2 \cdot C_6H_5$, orange needles, m. p. 80°, is produced from benzylamine and 3 : 5-*dinitro*-p-*tolyl*-p-*toluenesulphonate*, m. p. 152°.

4-*Chloro*-2 : 6-*dinitro*-1-*β-naphthylaminobenzene*, red needles, m. p. 201°, and 2 : 4-*dinitro*-1-*naphthylphenylamine*, red leaflets, m. p. 182°, can be similarly obtained from 4-chloro-2 : 6-dinitrophenol and β-naphthylamine and 2 : 4-dinitro-α-naphthol and aniline respectively by condensing the *p*-toluenesulphonates of these phenols with the appropriate amine. G. T. M.

Autoracemisation of Optically Active Ammonium Salts. Hans von Halban (*Ber.*, 1908, **41**, 2417—2421. Compare Abstr., 1907, ii, 246).—Wedekind and Paschke have recently attributed (this vol., i, 334) the diminution with time of the rotatory power of optically active ammonium salts in chloroform to autoracemisation, despite the fact that the author has shown (*loc. cit.*) that it is due to the decomposition of the ammonium salt into a tertiary amine and benzyl haloid. He has therefore examined by his method the behaviour of phenylbenzylmethylallylammonium bromide in chloroform, bromoform, and tetrachloroethane at the temperatures used by Wedekind and Paschke, and has obtained, for unimolecular reactions, values of K which agree fairly well with those given by these investigators. In some experiments the constant increases with time. The author cannot give a cause for this, but shows that it is not due to a reaction between the liberated amine and the solvent.

In answer to Wedekind's contention that active ammonium salts, which contain in addition to phenyl and benzyl only saturated groups, are remarkably stable in chloroform (Abstr., 1907, ii, 246), the author shows that the decomposition of phenylbenzyldiethylammonium bromide in chloroform increases with the time. C. S.

Double Dissociation of Quaternary Ammonium Compounds and a Convenient Synthesis of Iodoacetonitrile. Julius von Braun (*Ber.*, 1908, **41**, 2130—2144).—The reaction between bromoacetonitrile and dimethylaniline by which phenyltrimethylammonium bromide is formed (this vol., i, 676) is explained by a study of the interaction of dimethylaniline and iodoacetonitrile, as the latter is more reactive and a lower temperature can be employed. In this case an additive compound is first produced, which then decomposes according to the equation :

$$2NPhMe_2I \cdot CH_2 \cdot CN = NPhMe_3I + CH_2I \cdot CN + NPhMe \cdot CH_2 \cdot CN.$$

The additive compound is thus doubly dissociated into

$$NPhMe_2 + CH_2I \cdot CN$$

and $NPhMe \cdot CH_2 \cdot CN + CH_3I$, the first and fourth products of which at once unite. It is inferred that the analogous reaction with bromoacetonitrile proceeds in a similar manner. As the quaternary iodide is also obtained by the action of methyl iodide on methylanilinoacetonitrile, it is hence possible to convert half of the methyl iodide into iodoacetonitrile, and, by employing 2 mols. of methyl iodide in the reaction, 75% of the methylanilinoacetonitrile can be converted into iodoacetonitrile.

The author has employed iodoacetonitrile for the preparation of tertiary bases containing the cyanomethyl group, thus:

$$2R{\cdot}NMe_2 + CH_2I{\cdot}CN = R{\cdot}NMe_3I + R{\cdot}NMe{\cdot}CH_2{\cdot}CN.$$

In the case of tertiary diamines, three different compounds may be formed, according to the equations:

(1) $NMe_2{\cdot}X{\cdot}NMe_2 + CH_2I{\cdot}CN = NMe_3I{\cdot}X{\cdot}NMe{\cdot}CH_2{\cdot}CN.$

(2) $2NMe_2{\cdot}X{\cdot}NMe_2 + 2CH_2I{\cdot}CN = NMe_3I{\cdot}X{\cdot}NMe_3I + CN{\cdot}CH_2{\cdot}NMe{\cdot}X{\cdot}NMe{\cdot}CH_2{\cdot}CN.$

Phenyldimethylcyanomethylammonium iodide, $NPhMe_2I{\cdot}CH_2{\cdot}CN$, is a white, crystalline powder, m. p. 100° (decomp.). p-*Tolyldimethylcyanomethylammonium iodide*, m. p. 100° (decomp.), on heating yields iodoacetonitrile, *p*-tolyltrimethylammonium iodide, and methyl-*p*-toluidinoacetonitrile. *Phenylmethylcyanomethylethylammonium iodide*,

$$NPhMeEtI{\cdot}CH_2{\cdot}CN,$$

prepared from methylethylaniline and iodoacetonitrile, is a white, crystalline powder, m. p. 100° (decomp.). On heating, it undergoes triple dissociation, giving (1) $NPhMeEt + CH_2I{\cdot}CN$; (2) $NPhEt{\cdot}CH_2{\cdot}CN + MeI$, and (3) $NPhMe{\cdot}CH_2{\cdot}CN + EtI$.

Ethylanilinoacetonitrile and methyl iodide give phenyldimethylethylammonium iodide, m. p. 135° (Claus and Howitz, Abstr., 1884, 1005, give 126°). Methylanilinoacetonitrile and ethyl iodide interact only slowly, with formation of a small quantity of phenylmethyldiethylammonium iodide. On warming methylcyanoethylaniline,

$$NPhMe{\cdot}CHMe{\cdot}CN,$$

with methyl iodide, phenyltrimethylammonium iodide is produced.

By condensing iodoacetonitrile with dimethyltoluidine and with *p*-bromodimethylaniline, methyl-*p*-toluidinoacetonitrile and *p*-bromophenylmethylaminoacetonitrile respectively are obtained much more conveniently than by the method previously described (this vol., i, 625). p-*Iodophenylmethylaminoacetonitrile*, $C_6H_4I{\cdot}NMe{\cdot}CH_2{\cdot}CN$, prepared from iodoacetonitrile and *p*-iododimethylaniline, has m. p. 60°; in the same reaction is produced p-*iodophenyltrimethylammonium iodide*,

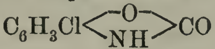
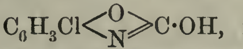
$$C_6H_4I{\cdot}NMe_3I,$$

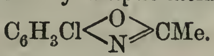
m. p. 212°.

β-Naphthylmethylaminoacetonitrile, $C_{10}H_7{\cdot}NMe{\cdot}CH_2{\cdot}CN$, prepared similarly from *β*-naphthyldimethylamine, has m. p. 76°. *Thallylaminoacetonitrile*, $OMe{\cdot}C_9NH_9{\cdot}CH_2{\cdot}CN$, prepared from methylthalline (Skraup, Abstr., 1886, 80), forms glistening crystals, m. p. 68°. When tetramethyldiaminodiphenylmethane is warmed with iodoacetonitrile, a mixture of tetramethyldiaminodiphenylmethane dimethiodide, the *methiodide* of the *trimethylcyanomethyl base*,

$$NMe_3I{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}NMe{\cdot}CH_2{\cdot}CN,$$

m. p. 172—173°, and *biscyanomethyldimethyldiaminodiphenylmethane*, $CH_2(C_6H_4{\cdot}NMe{\cdot}CH_2{\cdot}CN)_2$, m. p. 107°, is produced. The latter, which is also formed by the interaction of iodoacetonitrile and *s*-dimethyldiaminodiphenylmethane, is readily hydrolysed to the corresponding *dicarboxylic acid*, $CH_2(C_6H_4{\cdot}NMe{\cdot}CH_2{\cdot}CO_2H)_2$, sintering at 122°, m. p. 126°. *s*-*ω*-Dicyanotetramethylbenzidine is more conveniently prepared from iodoacetonitrile and tetramethylbenzidine than by the method previously given (this vol., i, 625). When 2 mols. of dimethylaniline are warmed with 1 mol. of iodoacetophenone, there are formed phenyl trimethylammonium iodide and methylanilinoacetophenone. No appreciable amount of the by-product obtained by Staedel and Siepermann (Abstr., 1880, 639) was formed; the author finds this to consist of *diphenacylaniline*, $NPh(CH_2\cdot COPh)_2$, m. p. 225°. Dimethylaniline with iodoacetamide (m. p. 95°: Henry, Abstr., 1885, 373, erroneously gives 157°) forms an *additive* compound, $MPhMe_2I\cdot CH_2\cdot CO\cdot NH_2$, m. p. 149°. J. C. C.

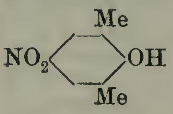
Preparation of 4-Chloro-2-aminophenol-5-sulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 194935).—On sulphonating 4-chloro-2-acetylaminophenol and hydrolysing the product, 4-chloro-2-aminophenol-6-sulphonic acid is formed, but when 4-chloro-1-hydroxybenzoxazole,  $C_6H_3Cl<^{-O-}_{NH}>CO$ or  $C_6H_3Cl<^{O}_{N}\geqslant C\cdot OH$, is subjected to this series of operations, 4-chloro-2-aminophenol-5-sulphonic acid is obtained. The sulphonation is effected with sulphuric acid, containing 10% of sulphur trioxide, and the hydrolysis with sodium hydroxide.

The new chloroaminophenolsulphonic acid furnishes a diazo-derivative crystallising in lustrous, yellow needles. This acid is also produced by successively sulphonating and hydrolysing 4-chloro-1-methylbenzoxazole,  $C_6H_3Cl<^{O}_{N}\geqslant CMe$. G. T. M.

Preparation of Aromatic Hydroxylated Nitro-compounds. RICHARD WOLFFENSTEIN and O. BÖTERS (D.R.-P. 194883).—The production of a nitrophenol has hitherto necessitated the preliminary introduction of a hydroxyl group into an aromatic nucleus, a process which is often somewhat difficult. It has now been found that the hydroxylation and nitration of an aromatic hydrocarbon may be effected simultaneously by the joint action of nitric acid and mercury, or a mercury compound. A mixture of benzene (400 grams), nitric acid (660 grams, D 1·48), and mercuric nitrate (150 grams) when heated on the water-bath yields 180 grams of picric acid, together with a certain amount of nitrobenzene. A similar experiment with double quantities of nitric acid furnished picric acid (380 grams), nitrobenzene (160 grams), and 2 grams of *o*-nitrophenol.

Naphthalene treated in this way gives rise to nitronaphthols and nitronaphthalene; toluene and benzoic acid furnish respectively trinitrocresol and nitrohydroxybenzoic acid. G. T. M.

***m*-2-Xylenol.** KARL AUWERS and TH. VON MARKOVITS (*Ber.*, 1908, 41, 2332—2340).—In connexion with their work on the oxidation of *m*-2-xylenol to tetramethyldiphenoquinone (Abstr., 1905, i, 219), the authors have prepared a number of new derivatives.



5-*Nitro*-m-2-*xylenol*, annexed formula, prepared by treating *m*-2-xylenol with nitric acid in glacial acetic acid solution, forms compact, colourless prisms, m. p. 169—170°. 5-*Nitroso*-m-2-*xylenol* is best obtained by acidifying a mixture of the phenol and sodium nitrite in dilute alkaline solution. It crystallises from benzene in yellow, glassy prisms and tablets, m. p. 170—171°. The *acetyl* derivative is a yellow, crystalline powder, m. p. 84—86°, 5-*Bromo*-m-2-*xylenol*, formed by bromination in acetic acid solution, crystallises in long, silky needles, m. p. 79·5°. 4 : 5-*Dibromo*-m-2-*xylenol*, obtained by brominating xylenol in presence of a trace of iodine or iron, forms small, colourless needles, m. p. 86—87°. By adding xylenol to excess of bromine, there is obtained 4 : 5 : 6-*tribromo*-m-2-*xylenol*, colourless needles, m. p. 200—201°. [The substance described under this name (Beilstein, *Handbuch*, 3rd Ed., **2**, 758) is really tribromo-*p*-xylenol.] 4-Bromo-*m*-2-xylenol is prepared by brominating 2-nitro-*m*-xylene and replacing the nitro-group by hydroxyl. 4-*Bromo*-2-*nitro*-m-*xylene*, prepared by adding iron powder to a cold mixture of 2-nitro-*m*-xylene and bromine, forms shining needles, m. p. 70—71°. On reduction with zinc dust and acetic acid, diazotisation of the resulting base, and allowing the diazo-solution to decompose at the ordinary temperature, 4-*bromo*-m-2-*xylenol* is formed; this crystallises from light petroleum in colourless, slender needles, m. p. 60—61·5°. If steam is led into the above-mentioned diazo-solution, 4-*bromo*-5-*nitroso*-m-2-*xylenol* is obtained; this forms pale yellow needles, m. p. 190—192°. 4-*Nitro*-m-2-*xylenol*, prepared from 4-nitro-*m*-2-xylidine by the diazo-reaction, has m. p. 99—100°.

m-2-*Xylenol methyl ether*, prepared by the use of methyl sulphate, is a colourless oil, b. p. 182°. With benzoyl chloride and aluminium chloride, it yields 4-*methoxy*-3 : 5-*dimethylbenzophenone*, m. p. 44°, which on warming with aluminium chloride gives 4-*hydroxy*-3 : 5-*dimethylbenzophenone*, colourless plates, m. p. 141—142°.

5-*Benzeneazo*-m-2-*xylenol* forms chrome-yellow prisms and tablets, m. p. 95—96°. J. C. C.

Phenolic Ethers containing the ψ-Allyl Side-chain $-CMe{:}CH_2$. III. Hydroxytoluic Series; Synthesis of Thymol. IV. Vanillic, Veratric, and Piperonylic Series. AUGUSTE BÉHAL and MARC TIFFENEAU (*Bull. Soc. chim.*, 1908, [iv], **3**, 729—732, 732—736).—A continuation of work on the synthesis of these esters (this vol., i, 261). Some of the data now given have been published before (Abstr., 1904, i, 742; 1905, i, 883). 3-ψ-*Allyl*-o-*cresol*,

$$OH\cdot C_6H_3Me\cdot CMe{:}CH_2,$$

D^{20} 1·040, n_D^{20} 1·543, b. p. 220—225°, obtained by the action of magnesium methyl iodide on methyl *o*-hydroxytoluate (m. p. 28—30°, b. p. 235°), has a characteristic thyme-like odour, gives a green coloration with ferric chloride, and with methyl sulphate yields the corresponding *methyl ether*, D^0 0·9901, D^{15} 0·9830, n_D^{15} 1·595, b. p. 217—218°, which, on reduction with sodium in alcohol, furnishes an iso*thymyl methyl ether*, $OMe\cdot C_6H_3Me\cdot CHMe_2$, D^0 0·9559, D^{19} 0·9430, n_D^{19} 1·50725, b. p. 210—213°. The latter on demethylation with hydriodic acid gives an iso*thymol*, D^0 0·9962, b. p. 228—230°, which does not crystallise when cooled. Methyl *m*-hydroxytoluate, D^0 1·1629, D^{21} 1·147, m. p. 27—28°, b. p. 118—122°/12 mm., 238—240°/760 mm., cannot be methylated by Graebe and Ullmann's process (*Ber.*, 1896, **29**, 824), but with methyl sulphate or iodide gives good yields of methyl *m*-methoxytoluate, D^0 1·1462, b. p. 259—261°/760 mm., and from the latter by the action of magnesium methyl iodide the *tertiary alcohol*, $OMe\cdot C_6H_3Me\cdot CMe_2\cdot OH$, D^0 1·0448, b. p. 129—130°/

11 mm., is obtained as a liquid, which, on distillation under atmospheric pressure, undergoes partial dehydration, yielding 3-*methoxy*-1-*methyl*-4-*ψ*-*allylbenzene*, D^0 0·9835, b. p. 216—219°. The latter can be prepared by heating the alcohol at 100° with acetic anhydride, a crystalline *polymeride*, D^0 1·0468, m. p. 56°, b. p. 215—223°/13 mm., being formed simultaneously. 3-Methoxy-1-methyl-4-ψ-allylbenzene on reduction with sodium in alcohol yields the methyl ether of thymol, which, on demethylation by hydriodic acid, or, better, with a mixture of hydrobromic and acetic acids, gives thymol.

Vanillyldimethylcarbinol, $OMe\cdot C_6H_3(OH)\cdot CMe_2\cdot OH$
$(OMe : OH : CMe_2\cdot OH = 3 : 4 : 1)$,
m. p. 55°, b. p. 165°/10 mm., obtained by the action of magnesium methyl iodide on ethyl vanillate, together with a *dimeride*, m. p. 174°, of ψ-eugenol, furnishes, on distillation at atmospheric pressure, a poor yield of ψ-eugenol, $OMe\cdot C_6H_3(OH)\cdot CMe\colon CH_2$ (Abstr., 1904, i, 742), m. p. 20°. The latter cannot be prepared directly by the action of magnesium methyl iodide on ethyl vanillate; it yields a crystalline benzoyl derivative, m. p. 58—59°.

Veratryldimethylcarbinol, $C_6H_3(OMe)_2\cdot CMe_2\cdot OH$ (*loc. cit.*), m. p. 78°, b. p. 140°/7 mm., 155°/13 mm., crystallises from light petroleum, and, on distillation under atmospheric pressure, furnishes ψ-methyleugenol, $C_6H_3(OMe)_2\cdot CMe\colon CH_2$, D^{20} 1·045, m. p. 36 (*loc. cit.*).

ψ-Safrole (1-ψ-allyl-3 : 4-catechol methylene ether), D^0 1·1338, D^{15} 1·1198, n_D^{15} 1·5619, b. p. 135°/20 mm., 233—239°/760 mm. (*loc. cit.*), obtained by the action of magnesium methyl iodide on methyl piperonylate, on reduction yields 1-*iso*propyl-3 : 4-catechol methylene ether, D^0 1·0935, n_D^{15} 1·52315, b. p. 225—230° (Abstr., 1905, i, 883), and, on oxidation with iodine and excess of yellow mercuric oxide, piperonylacetone, $CH_2\colon O_2\colon C_6H_3\cdot CH_2Ac$, D^0 1·2197, D^{22} 1·2035, n_D^{15} 1·54502, b. p. 163°/16 mm., 282—285°/760 mm. (compare Wallach, Abstr., 1904, i, 754); the *semicarbazone* of this has m. p. 159—160°. ψ-Safrole iodohydrin, on treatment with potassium hydroxide, yields an *ethylene oxide*, b. p. 150—155°/15 mm., which, on distillation under reduced pressure, yields 3 : 4-methylenedioxyhydratropaldehyde, b. p. 157—158°/16 mm., D^0 1·221 (compare Bougault, Abstr., 1901, i, 721); this yields a *semicarbazone*, of which the portion readily soluble in benzene has m. p. 156°, and that slightly soluble in the solvent, m. p. 158°.

T. A. H.

Derivatives of *p*-Nitrophenyl Mercaptan. Emil Fromm and J. Wittmann (*Ber.*, 1908, 41, 2264—2273. Compare Abstr., 1906, i, 656).—To obtain further insight into the nature of the solution of sulphur in alkali hydroxides, the action of *p*-chloronitrobenzene was studied, as this compound gives *p*-nitrophenyl mercaptan with potassium hydrosulphide (Willgerodt, Abstr., 1885, 519). The expected *p*-nitrophenylsulphoxide was, however, not obtained, but the interaction leads to the formation of sodium *p*-nitrophenoxide, 4 : 4′-dinitrodiphenyl disulphide (Willgerodt, *loc. cit.*), nitroaminodiphenyl sulphide (Kehrmann and Bauer, Abstr., 1897, i, 27), 4 : 4′-dinitrodiphenyl sulphide (Nietzki and Bothof, Abstr., 1895, i, 132), and the 4 : 4′-*dinitrodiphenyl ether* of *p*-azophenyl mercaptan, $N_2(C_6H_4\cdot S\cdot C_6H_4\cdot NO_2)_2$, m. p. 164°, which crystallises in golden-yellow needles from glacial acetic acid. Its constitution was determined by its conversion into thioaniline on reduction with tin and hydrochloric acid.

It has recently been shown that disulphides containing the grouping $-\ddot{C}-S\cdot S-\ddot{C}-$ lose sulphur on treatment with alkalis, water, or amines (Abstr., 1906, *loc. cit.*), but little is known at present of the action of alkalis on aromatic disulphides. The dinitrodiphenyl disulphide gives with alcoholic sodium hydroxide the sodium salt of *p*-nitrophenyl mercaptan and an insoluble *compound*, $C_{24}H_{26}O_4N_3S_2$?, which sinters at 130° and has m. p. 158°. As this is evidently not a direct product of the hydrolysis, the experiment was repeated with excess of benzyl chloride, when the benzyl ether of the mercaptan (m. p. 123°, Kulenkampff, *Diss.*, Freiburg, 1906) and benzoic acid were obtained. When less alkali and benzyl chloride are used, in addition to the above ether, *p*-nitrobenzenesulphinate is isolated, as well as a little nitrobenzene, showing that the hydrolysis proceeds on the same lines as that of phenyl disulphide (Schiller and Otto, this Journ., 1877, i, 463). The equation

$$2S_2(C_6H_4\cdot NO_2)_2 + 4KOH = 3NO_2\cdot C_6H_4\cdot SK + NO_2\cdot C_6H_4\cdot SO_2K + 2H_2O$$

is held not to explain the change; the first products are supposed to be mercaptan and the hypothetical compound, $NO_2\cdot C_6H_4\cdot SOH$, which acts as an oxidising agent.

Dinitrodiphenyl disulphide and ammonia, when heated in a closed tube, give nitroaminodiphenyl sulphide; this compound is not formed when the corresponding monosulphide is treated in a similar manner.

4 : 4′-*Dinitrodiphenylsulphone*, $C_{12}H_8O_6N_2S$, prepared by oxidising the sulphide with potassium dichromate and sulphuric acid, crystallises from glacial acetic acid; m. p. 282°. The corresponding *diamino*-derivative, $C_{12}H_{12}O_2N_2S$, forms white leaflets, m. p. 174°; its *diacetate*,

$$C_{16}H_{16}O_4N_2S,$$

white needles, m. p. 280°.

p-*Nitrophenylbenzylsulphone*, $C_{13}H_{11}O_4NS$, has m. p. 169° (Kulenkampff, *loc. cit.*, gives 149°). When heated with methyl iodide and alcoholic sodium hydroxide, *β-phenyl*iso*propylnitrophenylsulphone*, $NO_2\cdot C_6H_4\cdot SO_2\cdot CPhMe_2$, is formed, m. p. 169°.

The *mercaptal*, $C_{15}H_{14}O_4N_2S_2$, prepared from acetone and *p*-nitrophenyl mercaptan, forms white needles, m. p. 122°. By reducing the mercaptal from benzaldehyde and *p*-nitrophenyl mercaptan (Blanksma, Abstr., 1902, i, 282), the corresponding *diamino-mercaptal dihydrochloride*, $C_{19}H_{20}N_2Cl_2S_2$, is obtained. The *mercaptal*, $C_{19}H_{13}O_6N_3S_2$, from *p*-nitrobenzaldehyde forms white needles, m. p. 166°, and on reduction gives the *triamino-mercaptal trihydrochloride*, $C_{19}H_{22}N_3Cl_3S_2$; the *triacetate*, $C_{25}H_{25}O_3N_3S_2$, has m. p. 241°.

Nitrophenylmethanebisnitrophenylsulphone,

$$NO_2\cdot C_6H_4\cdot CH(SO_2\cdot C_6H_4\cdot NO_2)_2,$$

prepared from the trinitro-mercaptal by oxidation, forms light yellow leaflets, m. p. 235°. *p*-Nitrophenylthioglycine (Friedländer and Slubek, this vol., i, 525) is formed by the interaction of monochloroacetic acid and *p*-nitrophenyl mercaptan. W. R.

Arylsulphonated Acetonitriles. Action of Alkyl Haloids on Arylsulphon-ethenylamidoximes and -thioacetamides. JULIUS TRÖGER and BERNHARD LINDNER (*J. pr. Chem.*, 1908, [ii], 78, 1—20. Compare Abstr., 1905, i, 336).—The crystalline arylsulphonacetonitriles, $SO_2R\cdot CH_2\cdot CN$, described by Tröger and Hille (*loc. cit.*), are sparingly soluble in water, but dissolve readily in aqueous alkalis, forming metallic derivatives analogous to those of ethyl cyanoacetate and benzyl cyanide. Tröger and Vesterling (Abstr., 1905, i, 870) found that the action of alkyl haloids on the sodioarylsulphonacetonitriles leads to the formation of dialkyl derivatives, $SO_2R\cdot CR'_2\cdot CN$, which are even more stable towards hydrolysing agents, and form thioacetamides and amidoximes by addition of hydrogen sulphide and hydroxylamine (Tröger and Volkmer, Abstr., 1905, i, 356) with greater difficulty, than the parent nitriles. As the arylsulphonthioacetamides are readily soluble, whereas the corresponding acetamides are insoluble, in aqueous alkalis, it is considered that the thioacetamides react in the ψ-form, $SO_2R\cdot CH_2\cdot C(NH)\cdot SH$; this is in agreement with the formation of benzyl sulphide by the action of benzyl chloride on the sodium salts of the arylsulphonthioacetamides,

$$SO_2R\cdot CH_2\cdot C(NH)\cdot SNa,$$

the benzyl ether, $SO_2R\cdot CH_2\cdot C(NH)\cdot S\cdot CH_2Ph$, being considered to be formed intermediately. Similarly, it is probable that the alkali salts of the amidoximes have the constitution $SO_2R\cdot CH_2\cdot C(NH_2)\colon N\cdot OM'$. The present work was undertaken to determine in how far the arylsulphonthioacetamides and arylsulphonethenylamidoximes are capable of forming salts and ethers.

It is found that the amidoximes form stable salts only when the aryl nucleus contains a negative substituting group; if this is not the case, the alkali salt is readily hydrolysed, so that only mixtures of the salt and the free amidoxime can be obtained. The basic nature of the amidoxime group is shown by the solubility of the substances in mineral acids, and by the formation of acetyl derivatives. Whilst pure sodium salts are obtained only in certain cases, all the amidoximes studied form benzyl and methyl ethers containing the grouping $\colon N\cdot OR$. The arylsulphonthioacetamides, on the other hand, readily form stable sodium salts, but these on treatment with benzyl chloride react, forming benzyl sulphide and not ethers of the thioacetamides.

The *sodium* salt of *p*-bromophenylsulphonethenylamidoxime,

$$C_6H_4Br\cdot SO_2\cdot CH_2\cdot C(NH_2)\colon N\cdot ONa,$$

forms a yellowish-red, voluminous precipitate.

The following *benzyl ethers* of arylsulphonethenylamidoximes,

$$SO_2R\cdot CH_2\cdot C(NH_2)\colon N\cdot O\cdot CH_2Ph,$$

are described. The temperatures are melting points.

$R=Ph$: white leaflets, 114°; $R=p\text{-}C_6H_4Cl$: white needles, 114°; $R=p\text{-}C_6H_4Br$: white needles, 132—133°; $R=p\text{-}C_6H_4I$: white needles, 165°; $R=p\text{-}C_6H_4Me$: white prisms, 93°; $R=\alpha\text{-}C_{10}H_7$: white leaflets, 162°; $R=\beta\text{-}C_{10}H_7$: white leaflets, 129°; $R=o\text{-}C_6H_4\cdot OMe$: white needles, m. p. 94°; $R=p\text{-}C_6H_4\cdot OEt$: needles, 130°.

The *methyl ethers*, $SO_2R\cdot CH_2\cdot C(NH_2)\colon N\cdot OMe$, $R=\alpha\text{-}C_{10}H_7$: white crystals, m. p. 137°, and $R=\beta\text{-}C_{10}H_7$: yellow, sandy powder, m. p. 159° (slight decomp.), were prepared.

The following *acetyl* derivatives, $SO_2R\cdot CH_2\cdot C(NHAc)\colon N\cdot OR'$, are described.

$R = p\text{-}C_6H_4\cdot OEt$, $R' = CH_2Ph$: white needles, m. p. 115°; $R = p\text{-}C_6H_4Br$, $R' = H$: quadratic crystals, m. p. 193° (decomp.); $R = p\text{-}C_6H_4Me$, $R' = H$: white needles, m. p. 186°.

The *sodium* salts of phenylsulphonthioacetamide, $C_8H_8O_2NS_2Na$, *p*-tolylsulphonthioacetamide, $C_9H_{10}O_2NS_2Na$, and β-naphthylsulphonthioacetamide, $C_{12}H_{10}O_2NS_2Na$, were analysed. G. Y.

Acidity of the Different Phenolsulphonic Acids.

Julius Obermiller (*Zeitsch. anorg. Chem.*, 1908, **59**, 79—81).—According to Ley and Erler (compare this vol., i, 177), the acidity of the phenolic hydrogen atom of phenol-*o*-sulphonic acid is weaker than that of the phenolic hydrogen of the para-acid, and this is supposed to be in agreement with Ostwald's acidity rule for aromatic dicarboxylic acids. The author points out that it is doubtful whether the para-position is further removed than the meta- from the ortho-position.

The dimagnesium salt of phenol-*o*-sulphonic acid is hydrolysed to a much smaller extent that the corresponding salt of the para-acid, and this, in opposition to Ley and Erler, indicates that phenolic hydrogen in the ortho-position is the more strongly acidic. The greater tendency of the copper salt of the ortho-acid to form basic salts cannot be explained by the weaker acidity of the acid. The author's observations on the lead salts indicate that their tendency to yield basic salts increases with increasing acidity. In respect of this property, phenol-*o*-sulphonic acid is intermediate between the para-acid and the 2 : 4-disulphonic acid. H. M. D.

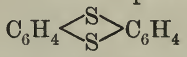
Condensation of Nitromalonaldehyde with Acetonylacetone. I.

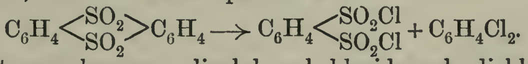
William J. Hale and Charles A. Robertson (*Amer. Chem. J.*, 1908, **39**, 680—696).—Hill and Hale (Abstr., 1905, i, 200) have shown that the sodium derivative of nitromalonaldehyde reacts with benzyl methyl ketone with formation of 5-nitro-2-hydroxydiphenyl. It was therefore expected that nitromalonaldehyde (2 mols.) would condense with acetonylacetone (1 mol.) to form a derivative of benzyl methyl ketone, and that the latter would react with a second mol. of the aldehyde with production of a diphenyl derivative. The present paper gives an account of a study of these reactions.

When a mixture of nitromalonaldehyde (2 mols.), acetonylacetone (1 mol.), and sodium hydroxide ($\frac{1}{8}$ mol.) was treated with carbon dioxide, a small quantity (17% of the theoretical) of 4-nitro-2-acetonylphenol separated, instead of the expected diphenyl compound. On acidifying the mother liquor with hydrochloric acid, a larger quantity (about 65%) of a light yellow, crystalline substance was obtained, the description of which is reserved for a future paper.

4-*Nitro-2-acetonylphenol*, $COMe\cdot CH_2\cdot C_6H_3(NO_2)\cdot OH$, m. p. 188·5° (corr.), forms needles or prisms; its *sodium* salt crystallises with $2H_2O$. The *methyl ether* has m. p. 60° (corr.), the *ethyl ether*, 70·5° (corr.), and the *oxime*, 146° (corr.). When the methyl ether is oxidised with potassium permanganate, methyl 5-nitrosalicylate is produced, showing that the acetonyl group is in the ortho-position to the hydroxyl group. 4:6-*Dinitro-2-acetonylphenol*, m. p. 121° (corr.), crystallises in lustrous plates; its *ethyl ether*, m. p. 118·5° (corr.), forms small, colourless prisms.

When 4-nitro-2-acetonylphenol is treated with nitromalonaldehyde in presence of a large excess of sodium hydroxide, 3:3′-*dinitro*-6:6′-*dihydroxydiphenyl*, $NO_2\cdot C_6H_3(OH)\cdot C_6H_3(OH)\cdot NO_2$, m. p. 301° (corr.), is produced, and crystallises in small, colourless needles. Its *dimethyl ether*, m. p. 264° (corr.), and *diethyl ether*, m. p. 271° (corr.), crystallise in needles. The *mono-ethyl ether*, m. p. 224° (corr.), obtained by the condensation of 4-nitro-2-acetonylphenyl ethyl ether with the sodium derivative of nitromalonaldehyde, forms silky needles. 3:3′-*Diamino*-6:6′-*dihydroxydiphenyl* is readily obtained by reducing the dinitro-compound with tin and hydrochloric acid; its *hydrochloride* forms long, colourless prisms. On oxidation with chromic acid, the diamino-compound is converted into diquinone, m. p. 192° (corr.) (compare Barth and Schreder, Abstr., 1885, 521). E. G.

Constitution of Thianthren [Diphenylene Disulphide]. J. J. B. Deuss (*Ber.*, 1908, **41**, 2329—2331).—The ortho-position of the sulphur atoms in diphenylene disulphide,  $C_6H_4{<}\genfrac{}{}{0pt}{}{S}{S}{>}C_6H_4$ (Graebe, Abstr., 1874, 469; 1876, i, 578), has been indicated by the work of Jacobson and Ney (Abstr., 1889, 771) and of Krafft and Lyons (Abstr., 1896, i, 297), whilst Genvresse (Abstr., 1897, i, 514) considered that the sulphur atoms were in the meta-position to each other. The author has treated diphenylene disulphone with phosphorus pentachloride, a reaction which proceeds thus:



$$C_6H_4{<}\genfrac{}{}{0pt}{}{SO_2}{SO_2}{>}C_6H_4 \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{SO_2Cl}{SO_2Cl} + C_6H_4Cl_2.$$

The products were benzene-*o*-disulphonyl chloride and *o*-dichlorobenzene, thus proving the ortho-position of the sulphur atoms in diphenylene disulphide. J. C. C.

Preparation of Carbamates of 2:6-Dialkyloxyphenols. Basler Chemische Fabrik (D.R.-P. 194034).—The carbamates of the 2:6-dialkyloxyphenols (pyrogallol 1:3-dialkyl ethers) are prepared by the following series of operations: (1) condensation of carbonyl chloride with either of these ethers in the presence of a tertiary base, such as pyridine or dimethylaniline, or with sodium salts alone; (2) treatment of these intermediate products with dry ammonia.

2:6-*Dimethoxyphenyl carbamate*, $C_6H_3(OMe)_2\cdot O\cdot CO\cdot NH_2$, is a white mass melting at 148—152°. G. T. M.

Three New Primary Alcohols Resulting from the Condensation of Sodium Benzyloxide with Propyl, Butyl, and *iso*Amyl Alcohols. Marcel Guerbet (*Compt. rend.*, 1908, **146**, 1405—1407).—The author has continued his work on the action of alcohols on sodium benzyloxide (this vol., i, 162). The alcohol already obtained from *n*-propyl alcohol has been proved to be *γ-phenyl*iso*butyl alcohol*, $CH_2Ph\cdot CHMe\cdot CH_2\cdot OH$. It is a colourless, oily liquid, b. p. 244—246°

(corr.), D_0^{20} 0·9841, with an odour recalling that of lilac. The *phenylcarbamate* forms colourless needles, m. p. 62—63°, and the *acetate* is a colourless liquid, b. p. 260—262° (corr.). On oxidation, the alcohol gives β-phenyl*iso*butyric acid. When sodium benzyloxide is condensed with *n*-butyl alcohol, there is formed *β-benzyl-*n*-butyl alcohol*, $C_6H_5{\cdot}CH_2{\cdot}CHEt{\cdot}CH_2{\cdot}OH$, a colourless, oily liquid with an odour resembling that of phenyl*iso*butyl alcohol; it has b. p. 258—261° (corr.) and D_0^{20} 0·9780. The *acetate* has b. p. 275—276° (corr.). On oxidation, the alcohol furnishes α-benzyl-*n*-butyric acid. The constitution of the benzylamyl alcohol prepared from *iso*amyl alcohol has not yet been established, but from analogy it is probably *β-benzyl*iso*butylcarbinol*, $CH_2Ph{\cdot}CH(C_3H_7){\cdot}CH_2{\cdot}OH$. It is a colourless, oily liquid, b. p. 272—274° (corr.), D_0^{20} 0·9687. The *acetate* has b. p. 279—281° (corr.). On oxidation, the alcohol yields *benzylvaleric acid*, $C_{12}H_{16}O_2$, a colourless, oily liquid with an odour of valerian, b. p. 305—308° (corr.). The *potassium*, *barium*, and *silver* salts are described. The *ethyl* ester has a strong, fruity odour; it has b. p. 274—276°. The *chloride* has b. p. 156—158°/22 mm. (corr.), and the *amide* has m. p. 94—95°. J. C. C.

Reduction with Platinum and Hydrogen. II. Dihydrocholesterol. Richard Willstätter and Erwin W. Mayer (*Ber.*, 1908, 41, 2199—2203. Compare this vol., i, 383; Windaus, Abstr., 1907, i, 610).—Cholesterol is reduced when hydrogen is passed through an ethereal solution of the substance containing platinum-black in suspension, yielding dihydrocholesterol (cholestanol), $C_{27}H_{48}O$, identical with the β-cholestanol obtained by Diels and Abderhalden (Abstr., 1906, i, 272) from cholestenone. This fact confirms the view of Diels and Linn (this vol., i, 164) that cholesterol and cholestenone contain the same ring complex. It follows from the values obtained for the rate of esterification of cholesterol and its dihydro-derivative that these compounds are secondary alcohols; further, as is to be expected, the absolute initial velocity of esterification of the saturated compound is greater than that of the unsaturated compound.

Dihydrocholesterol crystallises from light petroleum or acetone in prisms, m. p. 141·5—142° (corr.), and from dilute alcohol with $1H_2O$ in six-sided leaflets, which soften at 120°. The anhydrous substance in ether gives $[\alpha]_D^{22}$ +28·8°. At 18°, 100 parts of alcohol dissolve 1·60 parts of cholestanol and 2·28 parts of cholesterol.

Cholestanyl acetate, $C_{29}H_{50}O_2$, obtained by acting on the alcohol with acetic anhydride, crystallises in glittering prisms, m. p. 110·5—111° (corr.). W. H. G.

Connexion of Cholesterol and Cholic Acid with Camphor and Turpentine Oil. Hugo Schrötter and Richard Weitzenböck (*Monatsh.*, 1908, **29**, 395—398).—It was shown recently (this vol., i, 532) that, when treated with concentrated sulphuric acid and mercury and thereafter with nitric acid, cholesterol and cholic acid yield rhizocholic acid, which was considered to be hydroxy*cyclo*pentadienetricarboxylic acid. As this points to a relationship between cholesterol and cholic acid, on the one hand, and, on the other, the terpenes, which give analogously-constituted oxidation products, it was of importance to prepare rhizocholic acid in larger quantities and to establish its constitution. It is now found that rhizocholic acid is formed in small yields when camphor and turpentine oil are treated in the same manner as cholesterol with sulphuric acid and mercury and then with nitric acid. Apart from the question as to the correctness of the constitution suggested for rhizocholic acid, these results show that cholesterol and cholic acid are genetically related to camphor and turpentine oil, and must therefore belong to the terpene group. Thus, for the first time, is demonstrated the presence of a member of the terpene group amongst the degradation products of the animal organism.

G. Y.

Ergosterol and Fongisterol. CHARLES TANRET (*Compt. rend.*, 1908, **147**, 75—77).—Ergosterol is accompanied in spurred rye by a very similar crystalline substance, which also seems to exist in other fungi, and which the author designates *fongisterol*. The so-called ergosterol (Abstr., 1889, 407), having $[\alpha]_D$ −114°, contains one-ninth its weight of the new compound. Separation is effected by repeated recrystallisation from ether, ergosterol being the less soluble. Pure ergosterol, $C_{27}H_{42}O,H_2O$, is not efflorescent, and is completely dehydrated only at 105°, but the anhydrous substance quickly absorbs water from moist air. It crystallises from alcohol in wide, monoclinic lamellæ, and from ether in monoclinic needles. It has m. p. 165° (on Maquenne block), $[\alpha]_D$ −126° (in chloroform), −105·5° (in ether). The acetate has $[\alpha]_D$ −91·8° and m. p. 180·5°; the formate, $[\alpha]_D$ −97·9° and m. p. 161·5°.

Fongisterol, $C_{25}H_{40}O,H_2O$, is a lower homologue of ergosterol; it has a similar crystalline form, and is not efflorescent. It is dehydrated by chloroform, giving a milky liquid, but, when almost anhydrous, dissolves in 10 parts of this solvent at 20°. It has m. p. 144° (on Maquenne block), $[\alpha]_D$ −22·4° (in chloroform containing 2% of alcohol), −12·9° (in ether). The *acetate* has m. p. 158·5°, $[\alpha]_D$ −15·9° (in chloroform), −10·8° (in ether). The reactions with sulphuric acid and chloroform and with fuming nitric acid, previously indicated to distinguish ergosterol from cholesterol, serve to differentiate the latter from fongisterol.

When a particle of fongisterol is thrown on a few drops of 90% sulphuric acid, the latter acquires a ruby-red colour in a few seconds, which, after some minutes, changes into a reddish-violet. With ergosterol, a dirty red colour only appears at the end of one minute.

Ergosterol and fongisterol seem to be widely distributed. The cholesterols described by Gerard (Abstr., 1892, 1294; 1896, i, 21; 1898, i, 549) as belonging to the ergosterol group, probably consist of a mixture of these two compounds.

E. H.

Unsaponifiable Ingredients of Cocoa-Butter and their Detection in Butter. HERMANN MATTHES and EDWIN ACKERMANN (*Ber.*, 1908, **41**, 2000—2001).—The ethereal extract of cocoa-butter hydrolysed by alcoholic potassium hydroxide contains, in addition to ordinary phytosterol, a second alcohol, which gives the same colour reactions as phytosterol, but differs from it in taking up 2 mols. of bromine and in forming a sparingly soluble *tetrabromophytosteryl acetate*, $C_{33}H_{52}O_2Br_4$, m. p. 180—183° (decomp.). As butter contains only cholesterol, which does not form a tetrabromo-acetate, the authors are studying the practical application of the reaction to the detection of cocoa-fat in butter. Other fats of vegetable and of animal origin are being examined, in the hope that the reaction will differentiate between the two classes of fats. C. S.

Abnormal Products of the Fission of *cyclo*Hexanecarboxylic Acid. Nicolai D. Zelinsky and J. Gutt (*Ber.*, 1908, **41**, 2074—2076).—Whilst the corresponding hydrocarbons are readily obtained from aromatic and aliphatic acids by distillation of the calcium or barium salts with lime or soda-lime, such reactions are found in the *cyclo*hexane series to be accompanied by far-reaching complications. When distilled with sodium methoxide (Mai, Abstr., 1889, 1126), barium *cyclo*hexanecarboxylate yields a mixture of *cyclo*hexadiene with smaller amounts of *cyclo*hexene, together with dihydrotoluene, whereas, when heated with zinc chloride, *cyclo*hexanecarboxylic acid is converted chiefly into methyl*cyclo*pentane. It is shown that Einhorn's supposed methyl*cyclo*hexane, prepared by heating 1-methyl*cyclo*hexane-3-carboxylic acid with zinc chloride (Abstr., 1898, i, 407), is a mixture of that substance with an isomerisation product, probably dimethyl*cyclo*pentane. G. Y.

Characteristic Reaction of Anthranilic Acid. Bronislaw Pawlewski (*Ber.*, 1908, **41**, 2353—2354. Compare Suida, this vol., i, 523).—For the identification of anthranilic acid, Mohr and Köhler recommend its conversion into acetylanthranil (Abstr., 1907, i, 414). A still simpler method is now based on the formation of the characteristic *additive* compound of anthranilic acid and *p*-dimethylaminobenzaldehyde, $CO_2H\cdot C_6H_4\cdot NH_2,CHO\cdot C_6H_4\cdot NMe_2$, which is formed when the components are ground together and moistened with water or alcohol, or boiled with aqueous alcohol or benzene. If gently heated with aqueous alcohol or benzene, the acid and aldehyde form a yellow solution, which gradually deposits the red additive compound. This crystallises in needles, m. p. 180—182°, is decomposed partially on recrystallisation, or completely by ammonia, alkalis, alkali carbonates, or acids, and when treated with acetic anhydride yields *N*-acetylanthranilic acid, m. p. 180—181°. G. Y.

Preparation of Alkylaminoalkyl *p*-Aminobenzoates. Farbwerke vorm. Meister Lucius & Brüning (D.R.-P. 194748. Compare Abstr., 1907, i, 923).—*Chloroethyl 4-aminobenzoate*, white needles, m. p. 86—87°, obtained either by reducing *chloroethyl 4-nitrobenzoate*, needles, m. p. 56°, or by treating 4-aminobenzoic acid with ethylenechlorohydrin, furnishes *diethylaminoethyl 4-aminobenzoate*,

$$NH_2\cdot C_6H_4\cdot CO_2\cdot C_2H_4\cdot NEt_2,$$

m. p. 51°, hydrochloride, m. p. 156°, on heating with diethylamine at 110°. *Chloro*iso*propyl 4-aminobenzoate*, needles, 69°, hydrochloride, leaflets, m. p. 186°, obtained from *chloro*iso*propyl 4-nitrobenzoate*, brown oil, b. p. 195—196°/17 mm., gives rise to *piperidyl*iso*propyl 4-aminobenzoate*, m. p. 82°, on heating with piperidine at 120°.

A similar series of esters was obtained from *p*-nitrobenzoyl chloride and α-dichlorohydrin. The final product, *dipiperidylpropyl 4-aminobenzoate*, forms prismatic plates, m. p. 158°. G. T. M.

Preparation of Dialkylaminoalkyl Diaminobenzoates. Alfred Einhorn (D.R.-P. 194365).—*Diethylaminoethyl 3 : 4-diaminobenzoate*, $C_6H_3(NH_2)_2\cdot CO_2\cdot C_2H_4\cdot NEt_2$, oil, *hydrochloride*, needles, m. p. 163°, may be prepared from 3 : 4-diaminobenzoic or 3-nitro-4-aminobenzoic acid by the following alternative series of operations. The former of these acids, or its methyl ester, is either treated with diethylaminomethylcarbinol, $CH_2(NEt_2)\cdot CH_2\cdot OH$, or condensed successively with ethylene chlorohydrin and diethylamine. The intermediate *chloroethyl 3 : 4-diaminobenzoate* crystallises from benzene and petroleum in needles, m. p. 80°. The latter acid is condensed with ethylenechlorohydrin to *chloroethyl 3-nitro-4-aminobenzoate*, brownish-yellow needles or plates, m. p. 145—146°. Diethylamine converts this ester into *diethylaminoethyl 3-nitro-4-aminobenzoate*,

$$NO_2\cdot C_6H_3(NH_2)\cdot CO_2\cdot C_2H_4\cdot NEt_2,$$

yellow oil, *hydrochloride*, yellow needles, m. p. 208°, and this product, on reduction with tin and hydrochloric acid, furnishes the required ester of diaminobenzoic acid.

Diethylaminoethyl 3-amino-4-dimethylaminobenzoate,

$$NMe_2\cdot C_6H_3(NH_2)\cdot CO_2\cdot C_2H_4\cdot NEt_2,$$

oil, *hydrochloride*, needles, m. p. 164°, is derived by a similar series of operations from 3-nitro-4-dimethylaminobenzoic acid. These products are valuable anæsthetics of the novocaine series. G. T. M.

Optical Resolution of Aminophenylacetic Acid. Mario Betti and Mario Mayer (*Ber.*, 1908, 41, 2071—2073. Compare Abstr., 1907, i, 726; Ehrlich, this vol., i, 268; Fischer and Weichhold, *ibid.*, 419).—α-Aminophenylacetic acid has been resolved into its optically active constituents by means of *d*-camphorsulphonic acid and *d*-bromocamphorsulphonic acid.

l-*α-Aminophenylacetic acid* d-*camphorsulphonate*, $C_{18}H_{25}O_6NS$, separates from an aqueous solution of the two acids in colourless, trimetric, strongly refracting crystals, m. p. 210—212° (decomp.), $[\alpha]_D$ − 44·07°, and, on treatment with an alkali, yields *l*-α-aminophenylacetic acid, m. p. above 305°, $[\alpha]_D$ − 111·02°. *d*-α-Aminophenylacetic acid, obtained from the mother liquors, has $[\alpha]_D$ + 112·18°.

d-*α-Aminophenylacetic acid* d-*bromocamphorsulphonate*,

$$C_{18}H_{24}O_6NSBr,3H_2O,$$

separates from water as a crystalline mass, and loses $3H_2O$ at 65°, m. p. 200—210° (decomp.), $[\alpha]_D$ + 85·94°. The *d*-α-aminophenylacetic acid obtained from this has $[\alpha]_D$ + 110·60°. The *l*-α-aminophenylacetic acid obtained from the mother liquors has $[\alpha]_D$ − 107·20°.

Attempts to resolve aminophenylacetic acid by means of bornylamine were unsuccessful, as stable salts are not formed. G. Y.

Oxidation of *allo*-Cinnamic Acid. C. N. Riiber (*Ber.*, 1908, 41, 2411—2416).—The author confirms Fittig and Rür's statement that careful oxidation of cinnamic acid by dilute potassium permanganate yields the phenylglyceric acid, m. p. 141° (Abstr., 1892, 986), but considers it highly improbable that the substance obtained by Michael from *allo*-cinnamic acid in a similar manner and claimed by him to be the phenylglyceric acid, m. p. 121° (Abstr., 1902, i, 32), can in reality be such, since the method of isolation and the properties of the substance indicate that Michael was dealing with benzoic acid. A repetition of Michael's experiment has resulted in the isolation only of benzoic and oxalic acids.

Phenylglyceric acid, m. p. 121°, is obtained, however, when *methyl* allo-*cinnamate*, b. p. 49°/0·1 mm., prepared from the silver salt and methyl iodide, is oxidised in alcoholic alkaline solution at – 15° to – 17° by 0·5% potassium permanganate. C. S.

Liquid Crystals. TH. ROTARSKI (*Ber.*, 1908, **41**, 1994—1998).—The following substances are mentioned which form liquid crystals concerning which no statement is to be found in the literature of anisotropic liquids.

The anisotropic liquid phase of *p*-methoxycinnamic acid must be conditioned by the group $OMe\cdot C_6H_4\cdot CH{:}CH\cdot$, since the same phenomenon occurs with dianisyltetrylene,

$$OMe\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}CH\cdot C_6H_4\cdot OMe$$

(Fittig and Politis, Abstr. 1890, 770). Several investigators have prepared *p*-methoxycinnamic acid without mentioning the anisotropic character of the liquid form. The substance prepared by Perkin's method has m. p. 170°, the turbid liquid clarifying at 185°. After being heated ten times to 200°, the acid melts at 158° to a clear liquid, but, after purification, again shows its original m. p. and clarifying point (169° and 186° respectively). The ebullioscopic method indicates that *p*-methoxycinnamic acid in nitrobenzene exists in the bimolecular form; in this connexion it is worthy of note that the acid remains unchanged under conditions such as precipitation by water from its solution in cold concentrated sulphuric acid, distillation under ordinary pressure, and deposition by prolonged evaporation in sunlight of its solution in benzene, under which the various forms of unimolecular cinnamic acid and its polymerides, α- and β-truxillic acids, undergo conversion one into another. *p*-Methoxycinnamic acid is not affected by six hours' heating with water or 20% sodium hydroxide at 175—180°.

p-Methylaminobenzaldehydephenylhydrazone melts at 170° to a turbid liquid, which becomes clear at 190°; the corresponding ethyl derivative has 160° and 182° respectively (*Chem. Zentr.*, 1900, i, 1114).

s-Diethylbenzidine has m. p. 115·5°, the milky liquid clearing at 120·5° (Hofman, *Annalen*, 1860, **115**, 365; Tichwinski, Abstr., 1904, i, 267).

The cases of 4 : 4′-diphenylbismethyloldiphenyl,

$$OH\cdot CPh_2\cdot C_6H_4\cdot C_6H_4\cdot CPh_2\cdot OH,$$

m. p. 160°, clarifying point 186°, and its chloride, m. p. 219°, clarifying point 223°, have not been settled, since the author could not prepare the compounds, and the discoverer, Tschitschibabin (Abstr., 1907, i, 503), could not give a definite opinion.

p-*Methoxycinnamaldazine*, $N_2(:CH\cdot CH:CH\cdot C_6H_4\cdot OMe)_2$, obtained from *p*-methoxycinnamaldehyde and hydrazine sulphate in alkaline solution, separates from benzene in yellow crystals and gives a purple-red coloration with concentrated sulphuric acid. It melts at 210° and clarifies at 218°, but, owing to decomposition, the substance resolidifies without becoming turbid. C. S.

Clear, Transparent, Crystalline Liquids. DANIEL VORLÄNDER (*Ber.*, 1908, **41**, 2033—2052).—The view that the optical properties of turbid, crystalline liquids are merely due to suspensions or emulsions is rendered untenable, as it is now shown that perfectly clear, transparent liquids can exhibit similar optical properties, for example, double refraction. Such liquids behave exactly like a thin section of quartz or calcite cut at right angles to the principal axis.

The relationship between constitution and capacity for producing liquid crystals has been further examined (compare Abstr., 1906, i, 317, 1907, ii, 337, 442) by the inclusion of a number of substituted benzylideneamino-α-alkylated cinnamic esters, obtained by condensing the esters of α-substituted cinnamic acids with anisaldehyde, *p*-ethoxybenzaldehyde, and *p*-phenylbenzaldehyde.

[With W. KASTEN.]—The following esters have been examined: *Methyl* p-*methoxybenzylideneamino-α-methylcinnamate*, monotropic, crystalline liquid, but indication of 2 crystalline liquid phases when sufficiently cooled, m. p. 133°; *ethyl* ester, 1 enantiotrop. liq. cryst. phase, 2 solid phases, m. p. 89° and 93°; n-*propyl* ester, enantiotrop. cryst liq., 2 m. p., 50° and 85°; n-*butyl* ester, monotrop., m. p. 58°; iso*amyl* ester, monotrop., m. p. 46—47°; active *amyl* ester, 2 or 3 cryst. liq. phases, 1 enantiotrop. and 2 strongly circularly polarising, m. p. 60—63°.

Ethyl p-*methoxybenzylideneamino-α-ethylcinnamate* shows little tendency to form a crystalline liquid, and has m. p. 60—61°; the active *amyl* ester has not been obtained crystalline.

Ethyl p-*methoxybenzylideneamino-α-phenylcinnamate* does not form a crystalline liquid, and has m. p. 108°.

Methyl p-*ethoxybenzylideneamino-α-methylcinnamate*, 1 enantiotrop. cryst. liq. and 1 monotrop. cryst. liq. phase, 2 solid phases, m. p. 105° and 147°; *ethyl* ester, 1 enantiotrop. and 1 monotrop. cryst. liq. phase, both pseudoisotropic, 2 solid phases, indications of a third cryst. liq. phase, transition temperatures 124°, 94°, and 76°; n-*propyl* ester, 1 enantiotrop. and 1 monotrop. cryst. liq. phase, both pseudoisotropic, m. p. 88° and 121°; n-*butyl* ester, 2 cryst. liq. phases, enantiotrop. m. p. 55°, 65°, and 82°; iso*amyl* ester, enantiotrop. cryst. liq., m. p. 83° and 90°; active *amyl* ester, 3 cryst. liq. phases, 2 enantiotrop. m. p. 86° and 100°.

Ethyl p-*ethoxybenzylideneamino-α-ethylcinnamate*, 2 monotrop. cryst. liq. phases, both pseudoisotropic, 2 solid phases, transition temperatures 73°, 61°, and 45°; n-*propyl* ester, monotrop. cryst. liq., m. p. 98° and 63°; active *amyl* ester, 3 cryst. liq. phases, 2 strongly circularly polarising, m. p. 69°.

Ethyl p-*ethoxybenzylideneamino-α-*iso*propylcinnamate*, scarcely crystalline liquid, m. p. 76—77°.

Ethyl *p*-phenylbenzylideneaminocinnamate, 4 cryst. liq. phases, all enantiotrop., and under certain conditions pseudoisotropic, 1 in needles and 1 in rods, transition temperatures 216°, 207°, 204°, 178°, and 145°; n-*butyl* ester, 2 cryst. liq. phases, enantiotrop., m. p. 167° and 203°, liquid crystals from aqueous acetone; iso*amyl* ester, 2 cryst. liq. phases, enantiotrop., m. p. 164°, 188°, and 197°, liquid crystals from light petroleum; active *amyl* ester, 2 cryst. liq. phases, enantiotrop., m. p. 115°, 153°, and 180°.

Ethyl p-*phenylbenzylideneamino-α-methylcinnamate*, 3 cryst. liq. phases, all enantiotrop. and pseudoisotrop., m. p. 120°, 148°, and 175°; n-*butyl* ester, 2 or 3 liq. cryst. phases, enantiotrop., m. p. 100°, 136°, and 148°; active *amyl* ester, crystalline resin from aqueous acetone.

Ethyl phenylbenzylideneamino-α-ethyl cinnamate, 2 cryst. liq. phases, monotrop. and pseudoisotrop., 2 solid phases, m. p. 139°; n-*propyl* ester, 1 enantiotrop. cryst. liq. and 1 monotrop. cryst. liq. phase, both pseudoisotropic, m. p. 118° and 135°; active *amyl* ester, crystalline resin, clarifies at 118°.

Ethyl *p*-azocinnamate, 2 enantiotrop. cryst. liq. phases, m. p. 155—230°, at least 3 solid phases. *Ethyl* p-*azo-α-methylcinnamate*, monotrop. cryst. liq., m. p. 112°, 2 solid phases. Ethyl *p*-azoxycinnamate, enantiotrop. cryst. liq., m. p. 141° and 250°.

Ethyl p-*azoxy-α-methylcinnamate*, 2 or 3 enantiomorp. cryst. liq. phases, 3 or 4 solid phases, m. p. between 110° and 140°. *Ethyl β bromo*-p-*azoxy-α-methylcinnamate*, 2 pseudoisotrop. cryst. liq. phases, m. p. 110°. *Ethyl* p-*azoxy-α-ethylcinnamate*, m. p. 85°, scarcely crystalline liquid, and *ethyl* p-*azoxy-α-phenylcinnamate*, m. p. 154°, scarcely crystalline liquid.

The following general conclusions are drawn:

1. With the lengthening of the alkyl radicle of the CO_2R group, the tendency to form liquid crystals attains a maximum usually at the ethyl or *n*-propyl ester. 2. The radicles methoxyl, ethoxyl, and phenyl in the para-position strengthen the tendency to form liquid crystals; ethoxyl and phenyl have much the same effect, and this is greater than with methoxyl. 3. The tendency for liquid crystal formation is lessened by the introduction of alkyl groups in the α-position and in the order methyl, ethyl, phenyl. 4. The introduction of the optically active amyl radicle converts the crystalline liquid into a strongly circularly polarising condition.

The effect of β-substituents will be studied later. The rotation of some of the amyl esters is enormous. A mixture of amyl anisylideneaminocinnamate and amyl anisylideneamino-α-methylcinnamate in the crystalline liquid state has a rotatory power +5300° for sodium light and for a layer 1 mm. thick.

The molecules of the crystalline liquid may be regarded as arranging themselves in wavy rods, in long straight rods, or in short rods at right angles to the plates on which the drops are placed. In the last case, the pseudoisotropic form of Lehmann is obtained. Many of the new esters examined have this form, and are perfectly clear. Frequently when a turbid, crystalline liquid is rubbed with a needle or is pressed between glass plates, it becomes clear, and it is thus possible at will to obtain the clear or turbid, crystalline liquid condition.

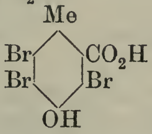
Certain esters appear clear when examined in any position; others, for example, ethyl and active amyl anisylideneaminocinnamate, are clear when examined in light which falls at right angles, but turbid when examined in reflected light or light at any other angle.

The crystalline liquids have been examined in many cases with the aid of the ultra-microscope, and also in converging polarised light. The result of the latter examination is to prove the uniaxial nature of the liquid crystals.

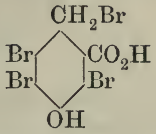
Measurements of the double refraction of many of the liquids have been made; the clear liquid esters of α-alkylated cinnamic acids are about twice as strongly refractive as calcite. J. J. S.

Hydroxytoluic Acids. II. 4-Hydroxy-*o*-toluic Acid. Theodor Zincke and M. Buff (*Annalen*, 1908, 361, 218—250).—It was shown previously (Abstr., 1907, i, 132) that 4-hydroxy-*o*-toluic acid forms a tribromo- (I) and a tetrabromo- (II) derivative and a perbromide, $(C_8H_4O_2Br_4)_2Br_2$.

(I.)

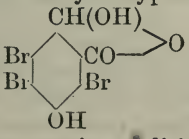


(II.)

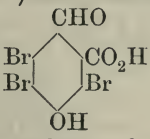


The action of an excess of bromine on the tribromo-derivative led to the formation of a mixture of compounds which could not then be separated. In some experiments, compounds were obtained which contained a smaller amount of bromine than the parent substance, and gave an intense yellow coloration with sodium carbonate. This led the authors to continue the investigation. It is now found that, in addition to the tetrabromo-acid and the perbromide, four new compounds are formed by the action of bromine on the tribromo-acid, the nature of the product depending, not on the excess of bromine, but on the presence or absence of moisture and on the temperature. In absence of moisture, the action of bromine on the tribromo-acid at 130—140° leads to the formation of the tetrabromo-acid and the perbromide, whilst at higher temperatures the product resinifies; but with a limited amount of moist bromine at 130—140°, the tribromo-acid yields a tribromohydroxyphthalide (III) or tribromoaldehydo-acid (IV). The intermediate formation of the tetrabromo-acid and of a tetrabromohydroxyphthalide (V) must be assumed.

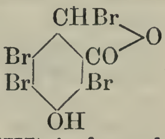
(III.)



(IV.)

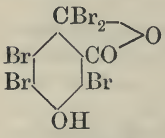


(V.)



Under certain conditions, a pentabromo-derivative (VI) is formed, which is converted by water into tribromo-4-hydroxyphthalic anhydride (VII); this is the chief product when slightly more moist bromine is employed for bromination of the tribromo-acid. The pentabromo-derivative (VI) is readily obtained by the action of bromine on tribromo-4-hydroxyphthalide (III) at 180—185°. Tribromo-4-hydroxyphthalic acid (VIII) is readily obtained from the pentabromo-compound (VI) or the tribromohydroxyphthalic anhydride (VII).

Tribromo-4-hydroxyphthalide (III) yields a diacetyl derivative and a ψ-methyl ester (IX). A normal ester (X) corresponding to this could not be obtained; the silver salt forms with methyl iodide the methyl ether (XI). The silver salt of this ether gives rise to a normal ester (XII) and a ψ-ester (XIII), which is formed also from the ψ-ester (IX).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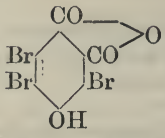
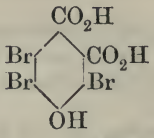

(VII.)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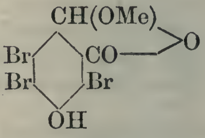
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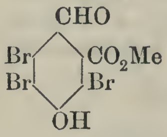
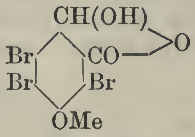
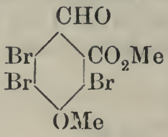
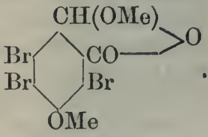
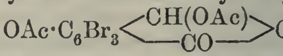

(X.)


(XI.)


(XII.)


(XIII.)

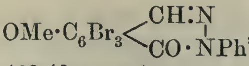
Tetrabromo-4-hydroxyphthalide (V) could not be obtained free from the aldehydo-acid; the mixture forms crystalline aggregates, m. p. 196°, and, when heated with methyl alcohol and sulphuric acid, yields the ψ-methyl ester of the aldehydo-acid.

The *tribromo-4-hydroxyaldehydo-acid*, (III) or (IV), crystallises from tetrachloroethane in colourless needles, m. p. 238° (decomp.), and, when heated with bromine at 170—175°, yields tribromo-4-hydroxyphthalic anhydride. The *diacetyl* derivative,  $OAc\cdot C_6Br_3<\begin{matrix}CH(OAc)\\CO\end{matrix}>O$, formed by the action of acetic anhydride and sulphuric acid on the aldehydo-acid, crystallises in white leaflets, m. p. 177—178°. The *ψ-methyl* ester (IX), prepared by heating the aldehydo-acid with methyl alcohol and sulphuric acid, forms needles, m. p. 232—233°, gives an intense yellow coloration when heated with phenylhydrazine in acetic acid, but crystallises unchanged on cooling, and forms an *acetyl* derivative $C_{11}H_7O_5Br_3$, needles, m. p. 179—180°.

The *ψ-dimethyl* ester (XIII), formed by the action of methyl iodide on the silver salt of the ψ-monomethyl ester, or by boiling the corresponding normal ester with methyl alcohol, crystallises in white needles, m. p. 184—185°, gives a yellow coloration when heated with phenylhydrazine in acetic acid, forms the acetyl derivative of the methyl ether when heated with acetic anhydride and sulphuric acid, and is hydrolysed with sodium hydroxide, forming the methyl ether.

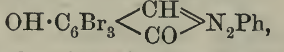
The normal *dimethyl* ester (XII) crystallises from benzene-light petroleum in prisms, m. p. 140—141°, and forms a *phenylhydrazine* derivative, $OMe\cdot C_6Br_3(CO_2Me)\cdot CH{:}N_2HPh$, which crystallises in yellow needles, m. p. 166—167°.

The *methyl ether* (XI), formed by the action of methyl iodide on the silver salt of the aldehydo-acid, or by hydrolysis of the two dimethyl esters, crystallises from benzene in leaflets, m. p. 202—203°, or from dilute methyl alcohol in needles, m. p. 216—218°, and forms an *acetyl* derivative, $C_{11}H_7O_5Br_3$, prisms, m. p. 188—189°. With phenyl-

hydrazine it forms a *derivative*,  $OMe\cdot C_6Br_3<\begin{matrix}CH:N\\ CO\cdot NPh\end{matrix}$, crystallising in colourless needles, m. p. 240—242° (decomp.).

With aniline in hot glacial acetic acid solution, the aldehydo-acid forms an *anilide*, $OH\cdot C_6Br_3(CO_2H)\cdot CH:NPh$, which crystallises in white needles, decomp. above 200°; this forms yellow salts, which are considered to have a quinonoid constitution. The alkali salts are decomposed by water, and form colourless solutions; the *aniline* salt, $O:C_6Br_3(CH\cdot NHPh)\cdot CO_2H,NH_2Ph$, forms a yellow, crystalline mass, and is decomposed by alkalis with formation of aniline.

3 : 5 : 6-*Tribromo-4-hydroxyphenylphthalazone*,

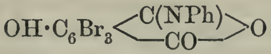
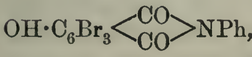


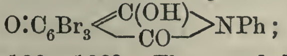
$$OH\cdot C_6Br_3<\begin{matrix}CH\\ CO\end{matrix}>N_2Ph,$$

formed from the aldehydo-acid and phenylhydrazine in glacial acetic acid solution, crystallises in white needles, m. p. 224—225°. The acetyl derivative, $C_{16}H_9O_3N_2Br_3$, white needles, m. p. 171°.

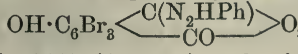
The *pentabromo-4-hydroxyphthalide* (VI) crystallises from benzene-light petroleum in white leaflets, m. p. 178—179°, and on hydrolysis with alkalis yields tribromo-4-hydroxyphthalic acid. The *acetyl* derivative, $C_{10}H_3O_4Br_5$, white needles, m. p. 158°. The action of methyl alcohol, aniline, and phenylhydrazine leads to the formation of the derivatives of the tribromo-anhydride.

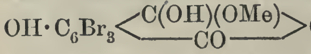
3 : 5 : 6-*Tribromo-4-hydroxyphthalic anhydride* (VII) is the final product of the action of moist bromine on tribromo-4-hydroxy-*o*-toluic acid, and is formed also by the action of moist bromine on tribromo-4-hydroxyphthalide, or of dry bromine on tribromo-4-hydroxyaldehydophthalic acid; it crystallises in stout prisms, m. p. 220°, dissolves in acetone or alcohol, forming a slightly yellow solution with fluorescence when dilute, and is slowly hydrolysed by boiling water, forming the corresponding acid. The anhydride forms yellow *alkali* and *aniline*, $C_{14}H_8O_4NBr_3$, salts, which are considered to have a quinonoid structure; the *pyridine* salt, $C_{13}H_6O_4NBr_3$, forms yellow crystals, m. p. 215—216°. The *acetyl* derivative, $C_{10}H_3O_5Br_3$, crystallises in white needles, m. p. 226°.

3 : 5 : 6-*Tribromo-4-hydroxyphthalanil*,  $OH\cdot C_6Br_3<\begin{matrix}C(NPh)\\ CO\end{matrix}>O$ or  $OH\cdot C_6Br_3<\begin{matrix}CO\\ CO\end{matrix}>NPh$, formed by the action of aniline on the pentabromo- or tribromo-4-hydroxyphthalic anhydride in glacial acetic acid solution, crystallises in yellow needles, m. p. 247—248°, and forms yellow salts, which are derived from the quinonoid form,



$$O:C_6Br_3<\begin{matrix}C(OH)\\ CO\end{matrix}>NPh;$$

the *aniline* salt, m. p. 182—183°. The *acetyl* derivative of the anil, white needles, m. p. 224—225°. *Tribromo-4-hydroxyphthalanilic acid*, $OH\cdot C_6Br_3(CO_2H)\cdot CO\cdot NHPh$, formed by boiling the phthalanil with alkalis, is obtained as a white, crystalline powder, m. p. 110—120°, and after resolidification, 240°. The *phenylhydrazone* of *tribromo-4-hydroxyphthalic anhydride*,  $OH\cdot C_6Br_3<\begin{matrix}C(N_2HPh)\\ CO\end{matrix}>O$, crystallises in yellow needles, m. p. 265—266° (decomp.), and with alkalis gives a yellow coloration and then a colourless solution, which becomes violet and gives a white precipitate with acids.

3 : 5 : 6-*Tribromo-4-hydroxyphthalic acid*, $C_8H_3O_5Br_3$, crystallises in white needles, m. p. 220°, after sintering at 100°, and forms colourless salts with alkalis and aromatic bases. The *methyl hydrogen* ester,  $\mathrm{OH\cdot C_6Br_3}<\substack{\mathrm{C(OH)(OMe)}\\ \mathrm{CO}}>\mathrm{O}$, is formed by the action of a limited amount of methyl alcohol and concentrated sulphuric acid on the anhydride; it crystallises in white needles, m. p. 130—140°, and after resolidification, 220°. The *dimethyl* ester,

$$\mathrm{OH\cdot C_6Br_3}<\substack{\mathrm{C(OMe)_2}\\ \mathrm{CO}}>\mathrm{O},$$

is prepared by the action of methyl iodide on the silver salt of the acid or of the methyl hydrogen ester, or of methyl alcohol on the pentabromo-anhydride; it crystallises in prisms, m. p. 148°, dissolves in alkalis, forming colourless solutions, and yields an *acetyl* derivative crystallising in leaflets, m. p. 124°. G. Y.

Combination of Benzilic Acid with Amines. Hans von Liebig (*J. pr. Chem.*, 1908, [ii], 78, 47—48).—When fused together, benzilic acid and phenols combine to form tritanic acids (this vol., i, 445, 540); in the same manner, benzilic acid combines with amines at 180—200°, the reaction leading at least in part to the formation of compounds of high molecular weight. Aniline and benzilic acid form a *compound*, $C_{60}H_{49}O_5N_3$, which crystallises from benzene in needles, m. p. 176°, is insoluble in aqueous sodium carbonate, and gives with concentrated sulphuric acid a brownish-red coloration rapidly becoming yellowish-brown. The composition of this product is that of 3 mols. of aminotritanic acid less 1 mol. of water.

Benzilic acid and *o*-toluidine form three *products*, which are insoluble in aqueous sodium carbonate:

(*a*) $C_{63}H_{55}O_5N_3$, crystallises in needles, m. p. 185°, is readily soluble in alcohol, gives a violet-brown coloration with concentrated sulphuric acid, and corresponds to the compound obtained from aniline.

(*b*) $C_{63}H_{48}O_3N_3$, crystallises in needles, m. p. 208°, is soluble in boiling alcohol, gives a lemon-yellow coloration with sulphuric acid, and in its composition is equivalent to 3 mols. of aminomethyltritanic acid less 3 mols. of water and 1 mol. of ammonia.

(*c*) The *lactam* of 2-amino-3-methyltritanic acid,

$$\mathrm{C_6H_3Me}<\substack{\mathrm{CPh_2}\\ \mathrm{NH}}>\mathrm{CO},$$

crystallises in needles, m. p. 278°, is insoluble in boiling alcohol, and gives a weak yellow coloration with sulphuric acid. G. Y.

Preparation of Anthroxanic Acid. Kalle & Co. (D.R.-P. 195812. Compare this vol., i, 421).—*o*-Nitromandelic acid or its salts are readily reduced by zinc dust and water even in the absence of ammonium chloride.

The aqueous solution when acidified after reduction yields the compound (nitrosomandelic acid?) melting at 130—135°; this product when treated with an alkali hydroxide passes into an alkali anthroxanate, which furnishes crystalline anthroxanic acid on treatment with acid. The reduction may be effected with other metals, providing that a temperature of 75° is not exceeded. G. T. M.

Preparation of Benzoylacetic Esters. ANDRÉ WAHL (*Compt. rend.*, 1908, **147**, 72—74).—Lœwig and Werdurann (*Ann. Phys. Chem.*, 1855, **50**, 95), by the action of sodium on cold ethyl benzoate, obtained a badly-defined, brown, resinous substance, which they called "hypobenzoylous acid." From this product the author has isolated benzoin, which is probably formed by reactions similar to those observed by Bouveault and Locquin (Abstr., 1905, i, 560) with aliphatic esters, thus:

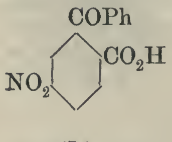
$$2PhCO_2Et + 4Na = ONa{\cdot}CPh{:}CPh{\cdot}ONa + 2NaOEt$$

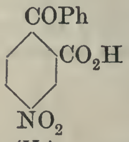
$$ONa{\cdot}CPh{:}CPh{\cdot}ONa + 2H_2O = 2NaOH + OH{\cdot}CPh{:}CPh{\cdot}OH \longrightarrow COPh{\cdot}CHPh{\cdot}OH.$$

Accordingly, addition of sodium to a mixture of ethyl acetate and benzoate may give rise to three reactions: (1) the action of sodium on ethyl acetate, giving ethyl acetoacetate; (2) that of sodium on ethyl benzoate, giving benzoin, and (3) that of the metal on the mixture of esters, producing ethyl benzoylacetate. In order that the last reaction shall predominate, it is necessary that the ethyl benzoate shall not come into contact with excess of sodium, whilst the latter must not meet with excess of ethyl acetate. Under these conditions, the yield is better than that obtained by Claisen and Lowman (Abstr., 1887, 583).

[With YOSHISAKA.]—Condensation of methyl benzoate with methyl acetate in the presence of sodium gives *methyl benzoylacetate*, $COPh{\cdot}CH_2{\cdot}CO_2Me$, an amber-coloured liquid, b. p. 152°/15 mm., D_4^0 1·173, which forms a *copper* salt as a yellowish-green, crystalline powder, m. p. 200—201°. *Methyl nitrosobenzoylacetate* forms colourless prisms, m. p. 140°; *methyl benzeneazobenzoylacetate*, yellow prisms, m. p. 76°; *methyl* p-*nitrobenzeneazobenzoylacetate* crystallises in yellow spangles, m. p. 148—149°; the corresponding *acid*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}C(CO_2H){\cdot}COPh$, forms yellow needles, m. p. 225—226° (decomp.). As in the case of the acetylacetic esters (Peters, Abstr., 1890, 1096), higher esters of benzoylacetic acid can be prepared from the methyl derivative by simple displacement. Thus, when methyl benzoylacetate is boiled with excess of *iso*butyl alcohol, iso*butyl benzoylacetate*, a light yellow liquid, b. p. 160°/12 mm., is formed. E. H.

m-**Nitro**-*o*-**benzoylbenzoic Acid.** JOSEF RAINER (*Monatsh.*, 1908, **29**, 431—437).—The condensation of 4-nitrophthalic anhydride with benzene in presence of aluminium chloride was found to lead to the formation of two nitrobenzoylbenzoic acids (this vol., i, 539), one of which is identical with Kliegl's acid (Abstr., 1905, i, 187), and is therefore 4-nitro-2-benzoylbenzoic acid (I). The isomeride, which is formed in the larger amount, must be 5-nitro-2-benzoylbenzoic acid (II).


(I.)


(II.)

5-Nitro-2-benzoylbenzoic acid crystallises from methyl alcohol in quadratic leaflets containing CH_4O, or from water in needles, m. p. 212°. The *silver* salt, $C_{14}H_8O_5NAg$, was analysed. The *methyl* ester, prepared by boiling the acid with methyl alcohol and sulphuric acid, crystallises in hexagonal prisms, m. p. 123·5—124°, and gives only a faint yellow coloration with concentrated sulphuric acid. The isomeric *ψ-ester* (compare Goldschmiedt and Lipschütz, Abstr., 1904, i, 168; 1905, i, 132; Meyer, Abstr., 1904, i, 747; 1905, i, 133), obtained by converting the acid into its *chloride* by means of thionyl chloride and treating the product with methyl alcohol in chloroform solution, has m. p. 104—105°, and gives an intense, yellow coloration with concentrated sulphuric acid. When heated with concentrated sulphuric acid, 5-nitro-2-benzoylbenzoic acid condenses to 2-nitroanthraquinone (Kliegl, *loc. cit.*).

5-*Amino-2-benzoylbenzoic acid*, $C_{14}H_{11}O_3N$, formed by reduction of the nitro-acid with ferrous sulphate and ammonia, crystallises in yellow, rhombic needles, m. p. 193—194° (decomp.), or 195—196° in a sealed capillary tube, and forms a crystalline *silver* salt. G. Y.

Preparation of Acylbenzoic Acids from Phthalic Anhydride, Hydrocarbons, and Aluminium Chloride. Gustav Heller (D.R.-P. 193961).—The higher hydrocarbons, such as naphthalene or anthracene, do not readily condense with phthalic anhydride in the presence of aluminium chloride, but when allowed to react in the presence of benzene, toluene, or xylene, an excellent yield of naphthoylbenzoic or anthracylbenzoic acid is obtained. The reaction goes in this sense when the calculated amount of higher hydrocarbon is employed, even although the benzenoid hydrocarbon may be in excess. Apparently, naphthalene or anthracene displaces benzene in the additive compound produced from the latter hydrocarbon with phthalic anhydride and aluminium chloride. G. T. M.

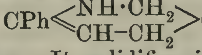
Preparation of Methylthiosalicylic [*o*-Methylthiolbenzoic] Acid. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 193800).—By treating sodium dithiosalicylate with methyl sulphate in methyl-alcoholic solution, a poor yield of methyl *o*-methylthiolbenzoate is obtained, but on boiling an alkaline solution of the dithio-acid with sodium methyl sulphate, the reaction only goes as far as the production of the monomethyl derivative. The addition of dilute acid to the solution sets free *o*-methylthiolbenzoic acid, $SMe{\cdot}C_6H_4{\cdot}CO_2H$, b. p. 168—169°. G. T. M.

δ-Aminoketone Derivatives. Siegmund Gabriel (*Ber.*, 1908, **41**, 2010—2014. Compare this vol., i, 464, and following abstract).——α- and β-Aminoketones are fairly stable, whereas γ-aminoketones readily lose water, yielding phenylpyrroline derivatives. It is now shown that δ-aminoketones are also unstable and readily yield anhydro-derivatives.

δ-Phthaliminovaleric acid, $C_8H_4O_2{:}N\cdot[CH_2]_4\cdot CO_2H$, is obtained when ethyl γ-phthaliminomalonate is hydrolysed with hydriodic acid and the resulting acid heated at 168°; it crystallises from water in rectangular plates, m. p. 117°. The corresponding *chloride*,

$$C_8H_4O_2{:}N\cdot[CH_2]_4\cdot COCl,$$

crystallises from light petroleum in snow-white plates, m. p. 78—81°, and condenses with benzene in the presence of aluminium chloride, yielding *δ-phthaliminovalerophenone*, $C_8H_4O_2{:}N\cdot[CH_2]_4\cdot COPh$, which crystallises from alcohol in long, colourless prisms, m. p. 94—95°.

When hydrolysed with glacial acetic and fuming hydrochloric acids at 138°, the phthaliminoketone yields the anhydride, *2-phenyltetrahydropyridine*,  $\mathrm{CPh}\!\left<\begin{matrix}\mathrm{NH\cdot CH_2}\\ \mathrm{CH{-}CH_2}\end{matrix}\right>\!\mathrm{CH_2}$, in the form of an oil, b. p. 275—277°/751·5 mm. It solidifies in a freezing mixture, and has m. p. 18°. The *hydrochloride* crystallises from fuming hydrochloric acid in colourless needles, m. p. 86—87°. The *platinichloride* forms orange-red, hexagonal plates; it sinters at 190° and melts at 191—192°, and solidifies and melts again at 202°. The *aurichloride* melts at 118°, after sintering at 110°. The *picrate*, $C_{17}H_{16}O_7N_4$, crystallises in long, yellow needles, m. p. 181°, after sintering at 160°.

When reduced with tin and hydrochloric acid, the base yields *2-phenylpiperidine.* This separates from its aqueous solution in colourless crystals containing $1H_2O$. The hydrate melts at 60—61° to a turbid liquid, and, when further heated, loses water and yields the anhydrous base, $C_{11}H_{15}N$, in the form of an oil, b. p. 255—255·5°/767 mm.

The *hydrochloride* crystallises in hard needles, m. p. 196—197°; the *platinichloride* has m. p. 197°; the *aurichloride* has m. p. 159—160° and the *picrate* m. p. 115—116°. J. J. S.

ε-Amino-ketones. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1908, 41, 2014—2017. Compare preceding abstract).—ε-Aminoketones, unlike the corresponding γ- and δ-compounds, appear to be stable; they do not readily form anhydro-derivatives.

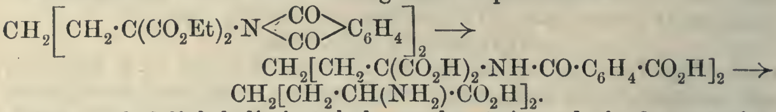
Ethyl phthaliminobutylmalonate (Gabriel and Maass, Abstr., 1899, i, 595), when hydrolysed with hydriodic acid and the resulting dibasic acid heated at 160°, yields *ε-phthaliminohexoic acid*,

$$C_8H_4O_2{:}N\cdot[CH_2]_5\cdot CO_2H,$$

m. p. 107—107·5°. The corresponding *chloride*, $C_8H_4O_2{:}N\cdot[CH_2]_5\cdot COCl$, melts at about 60°, and readily yields *ε-phthaliminohexophenone*, $C_8H_4O_2{:}N\cdot[CH_2]_5\cdot COPh$, which crystallises from dilute alcohol in colourless plates, m. p. 90—91°. When hydrolysed at 138° with acetic and hydrochloric acids, it yields *ε-aminohexophenone*, $COPh\cdot[CH_2]_5\cdot NH_2$, in the form of an oil. The *hydrochloride* has m. p. 153—154°; the *platinichloride* forms flat plates, and has m. p. 213° (decomp.). J. J. S.

Synthesis of Amino-acids. VIII. Diaminodicarboxylic Acids and Hydroxyamino-acids. SÖREN P. L. SÖRENSEN and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1908, 56, 250—304).—Fuller details for the preparation of αδ-diaminoadipic, α-amino-γ-hydroxybutyric, and αε-diaminopimelic acids are given (compare Abstr., 1905, i, 600). A 90% yield of diaminopimelic acid can be obtained by hydrolysing ethyl phthaliminotrimethylenedimalonate with sodium hydroxide and evaporating the product with hydrochloric acid.

The reactions which occur during the two processes are:

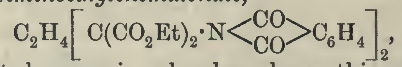


$$CH_2\left[CH_2\cdot C(CO_2Et)_2\cdot N{<}\substack{CO\\CO}{>}C_6H_4\right]_2 \longrightarrow CH_2[CH_2\cdot C(CO_2H)_2\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H]_2 \longrightarrow CH_2[CH_2\cdot CH(NH_2)\cdot CO_2H]_2.$$

When ethyl diphthaliminoethylenemalonate is used, the first reaction proceeds in a similar manner, and a good yield of the corresponding phthalamic acid, $C_2H_4[C(CO_2H)_2\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H]_2$, is obtained. If this is evaporated with hydrochloric acid, the yield of diaminoadipic acid is small, as secondary reactions occur. The yield can be considerably increased by first heating the hexabasic acid at 100—105° for twenty-four hours, when carbon dioxide and a little phthalic acid are formed, and then hydrolysing with barium hydroxide and evaporating with hydrochloric acid.

In the reaction between ethyl sodiophthaliminomalonate and ethylene bromide, the yield of ethyl diphthaliminoethylenemalonate is small. Among other products formed is the lactone of ethyl phthalimino-β-hydroxyethylmalonate, obtained by the elimination of ethyl bromide from the intermediate product, ethyl phthalimino-β-bromoethylmalonate. The lactone provides a convenient material for the preparation of α-amino-γ-hydroxybutyric acid, which can be isolated in the form of its sparingly soluble benzoyl derivative. The ethyl diphthaliminoethylenemalonate is readily separated from the lactone by shaking with normal sodium hydroxide solution at the ordinary temperature and then for half-an-hour on the water-bath. Under these conditions, the lactone is dissolved, and the solution may be used for the preparation of α-amino-γ-hydroxybutyric acid.

Ethyl diphthaliminoethylenemalonate,



$$C_2H_4\left[C(CO_2Et)_2\cdot N{<}\substack{CO\\CO}{>}C_6H_4\right]_2,$$

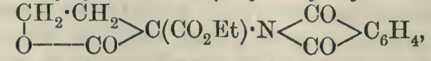
crystallises from benzene in colourless, long, thin prisms or compact crystals, m. p. 209—210°, and is insoluble in water, ether, or light petroleum. The corresponding *phthalamic acid*,

$$C_2H_4[C(CO_2H)_2\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H]_2,$$

separates from solutions of its sodium salt on the addition of well-cooled hydrochloric acid in the form of compact, rectangular crystals containing $2H_2O$. When quickly heated, it has m. p. 240° (decomp.), but also decomposes at 210°.

αδ-Diaminoadipic acid is practically insoluble in the ordinary neutral solvents, but dissolves in 5*N*-sulphuric or hydrochloric acid; it does not melt at 275°, but, when heated for some time at this temperature, slowly decomposes. Its *dibenzoyl* derivative has m. p. 270—275°, and is sparingly soluble in all ordinary solvents.

The *lactone* of *ethyl phthalimino-β-hydroxyethylmalonate*,



$$\begin{array}{l}CH_2\cdot CH_2\\ |\\ O\text{——}CO\end{array}{>}C(CO_2Et)\cdot N{<}\substack{CO\\CO}{>}C_6H_4,$$

crystallises from alcohol in flat prisms, m. p. 132°. When the alkaline solution is evaporated with hydrochloric acid, it yields α-amino-γ-hydroxybutyrolactone, the benzoyl derivative of which has m. p. 145° (compare Fischer and Blumenthal, Abstr., 1907, i, 191). The dibenzoyl derivative of α-amino-γ-hydroxybutyric acid can be obtained from the oily products formed in the preparation of ethyl diphthaliminoethylenemalonate, and has m. p. 210—211°.

Ethyl diphthaliminotrimethylenemalonate crystallises from absolute alcohol in flat, lens-shaped needles, m. p. 149°. *αε-Diaminopimelic acid*, $C_7H_{14}O_4N_2$, crystallises from aqueous alcohol in slender needles, it does not melt at 300°, and has no sweet taste. It is readily precipitated by phosphotungstic acid. Its *dibenzoyl* derivative, $C_{21}H_{22}O_6N_2$, crystallises from 25% alcohol in minute needles, m. p. 220°.

The benzoylation of certain aminohydroxy- and diamino-acids has been studied under varying conditions. When an excess of sodium hydroxide is used, so that the liquid during the process is always about $0·5N$ as regards the alkali, it is found that aminohydroxy-acids yield monobenzoyl derivatives only. When, on the other hand, the solution is kept practically neutral, a mixture of mono- and di-benzoyl derivatives is obtained. The benzoyl derivatives of hippuric acid and of diamino-acids are not affected by warming with $N/20$-sodium hydroxide solution; under the same conditions, the dibenzoyl derivatives of aminohydroxy-acids are hydrolysed to monobenzoyl derivatives.

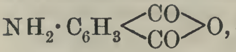
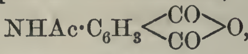
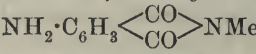
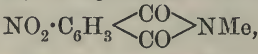
Monobenzoyl α-amino-δ-hydroxyvaleric acid has been obtained in a crystalline form with m. p. about 170°.

Monobenzoyl α-amino-γ-hydroxyvaleric acid has m. p. about 138° (Fischer and Blumenthal, *loc. cit.*, 121°). Its barium salt is sparingly soluble. J. J. S.

4-Amino-*o*-phthalic Acid and Some of its Derivatives. Marston T. Bogert and Roemer Rex Renshaw (*J. Amer. Chem. Soc.*, 1908, **30**, 1135—1144).—In an earlier paper (Abstr., 1906, i, 510), methyl 4-aminophthalate and some of its derivatives were described. A description is now given of the acid, its salts, and certain derivatives.

It has been found by Miller (Abstr., 1882, 404) that on reducing 4-nitrophthalic acid with tin and hydrochloric acid and treating the product with hydrogen sulphide, *m*-aminobenzoic acid is produced; this result is now confirmed. The method described by Seidel (Abstr., 1902, i, 160) for preparing 4-aminophthalic acid by reducing the nitro-compound with sodium sulphide does not readily afford a good yield. The acid can be easily prepared, however, by the hydrolysis of the dimethyl ester or of 4-nitrophthalimide.

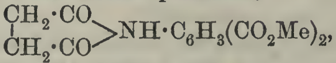
4-Aminophthalic acid forms colourless, microscopic plates; when heated, it loses water and changes into a yellowish-grey, infusible residue. If the acid is boiled with hydrochloric acid, it is converted into *m*-aminobenzoic acid. On diazotising 4-aminophthalic acid and adding the product to a warm copper potassium cyanide solution, a yellow, granular *compound*, m. p. 166° (corr.), is produced, which is probably the 4-monoamide of trimellitic acid, and small quantities of another substance, possibly trimellitic acid, are formed simultaneously.

The *hydrochloride* of 4-aminophthalic acid, the *sodium*, *potassium*, *ammonium*, *calcium*, *barium*, *nickel*, *copper*, *lead*, and *silver* salts, and the *mercuric chloride* double salt are described. The *anhydride*,  $NH_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{CO}{CO}>O$, obtained by heating the acid at 180—200° for two hours, is a pale salmon-coloured, infusible solid. 4-*Acetylaminophthalic anhydride*,  $NHAc\cdot C_6H_3<\genfrac{}{}{0pt}{}{CO}{CO}>O$, m. p. 206—207° (corr.), obtained by the action of acetic anhydride or acetyl chloride on the amino-acid, forms microscopic needles. 4-*Aminophthalimide*, m. p. 294° (corr.), prepared by reducing 4-nitrophthalimide with stannous chloride, crystallises in golden-yellow needles; its *hydrochloride* forms grey crystals. The *methylimide*,  $NH_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{CO}{CO}>NMe$, m. p. 242—243° (corr.), forms yellow crystals; its *hydrochloride* crystallises in plates. 4-*Nitrophthalmethylimide*,  $NO_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{CO}{CO}>NMe$, m. p. 179—180° (corr.), forms long, white needles. 4-*Aminophthalanil* has m. p. 205·5° (corr.). The *carbamide* derivative of the methyl ester,

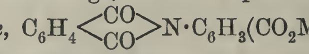
$$CO[NH\cdot C_6H_3(CO_2Me)_2]_2,$$

m. p. 213—214° (corr.), prepared by the action of carbonyl chloride on a pyridine solution of the methyl ester, crystallises in short needles.

Methyl 4-ethyloxalylaminophthalate (Abstr., 1906, i, 510) has m. p. 126° (corr.). *Methyl* 4-*succiniminophthalate*,



$$\genfrac{}{}{0pt}{}{CH_2\cdot CO}{CH_2\cdot CO}>NH\cdot C_6H_3(CO_2Me)_2,$$

m. p. 153·4° (corr.), forms large, colourless prisms or needles. *Methyl* 4-*phthaliminophthalate*,  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot C_6H_3(CO_2Me)_2$, m. p. 174° (corr.), crystallises in long, colourless needles. E. G.

Constitution of Phthalein Salts. RICHARD MEYER and KARL MARX (*Ber.*, 1908, 41, 2446—2453).—The results published previously (Abstr., 1907, i, 932) have been confirmed. The absorption spectra of aqueous solutions of the sodium salts of phenolphthalein, tetrabromophenolphthalein, quinolphthalein, fluorescein, and eosin have been compared. The curves obtained on plotting the concentrations against the wave-lengths are similar for all five compounds. The conclusion is drawn therefore that the salts of these substances must have a similar quinonoid structure, the difference in colour being merely one of degree.

The *potassium* salt of phenolphthalein, $C_{20}H_{12}O_4K_2$, forms a deliquescent, deep red mass; the *sodium* salt, $C_{20}H_{12}O_4Na_2$, is almost black with a metallic glance. W. H. G.

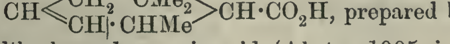
Theory of Indicators. SALOMON F. ACREE (*Amer. Chem. J.*, 1908, 39, 649—650). JULIUS STIEGLITZ (*ibid.*, 651—653).—With reference to this controversy (compare Abstr., 1904, ii, 17; this vol., i, 423), the authors, starting from different points of view, have now come to similar conclusions regarding the theory of indicators. These conclusions have been already put forward (this vol., i, 423). E. G.

Theory of Indicators and the Reactions of Phthaleins and their Salts. II. Salomon F. Acree and E. A. Slagle (*Amer. Chem. J.*, 1908, **39**, 789—791).—Acree (this vol., i, 423) has stated that the chief source of the colour of salts of the phthaleins is the phenol salt of a quinone compound.

It is now pointed out that Orndorff has obtained coloured salts of trimethylgallein and its tetrachloro-derivative, whilst such substances as phenolphthalein methyl ether and tetrabromophenolphthalein ethyl ether dissolve in alkalis to form colourless solutions. The sodium salt of fluorescein ethyl ether yields an aqueous solution which is much less intensely coloured than are solutions of fluorescein salts. The alcoholic solution of this salt is only faintly coloured at from − 15° to 0°, but the colour increases as the temperature is raised to 80°, and decreases again as the temperature is lowered. When this sodium salt is treated with ethyl iodide, it yields a mixture of the colourless phenolic diethyl ether and the coloured quinonoid diethyl ether.

All these facts are discussed in the light of Acree's theory (*loc. cit.*), and are shown to be readily capable of explanation. E. G.

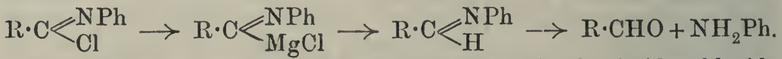
Conversion of Carboxylic Acids into their Aldehydes. Georg Merling (*Ber.*, 1908, **41**, 2064—2066).—In the course of his studies on the synthesis of perfumes, the author has repeatedly found it necessary to convert hydroaromatic acids into the corresponding aldehydes. As the reactions employed previously for such conversion give only poor yields and are therefore unsuitable for the purpose, a new method was required. One giving in the case of hydroaromatic acids 50% to 80% yields of the aldehyde has now been found in the following series of changes. The carboxylic acid, $R\cdot CO_2H$, is converted by way of the chloride, $R\cdot COCl$, anilide, $R\cdot CO\cdot NHPh$, and phenylimide chloride, $R\cdot CCl\colon NPh$, into the diphenylamidine, $R\cdot C(NPh)\cdot NHPh$, which is reduced by means of sodium and alcohol to the diphenylmethylenediamine, $R\cdot CH(NHPh)_2$; this, when heated with dilute mineral acids, is hydrolysed, forming the aldehyde, $R\cdot CHO$, and aniline. The method is less suitable for the formation of aldehydes from aromatic or aliphatic acids; benzaldehyde is obtained from benzoic acid in only a 20% yield, whilst with many aliphatic acids the yield of aldehyde is still smaller. The amount of aldehyde formed appears to depend on the stability of the diphenylmethylenediamine; in many cases, this is decomposed by the reducing agent with formation of the Schiff's base, $R\cdot CH\colon NPh$, which is then further reduced, and hence does not yield the aldehyde on hydrolysis.

Δ^3-cyclo*Geranic acid*,  $CH\left<\begin{array}{l}CH_2{-}CMe_2\\ CH|\cdot CHMe\end{array}\right>CH\cdot CO_2H$, prepared by fission of water from ketodihydro*cyclo*geranic acid (Abstr., 1905, i, 349), is obtained in two stereoisomeric forms, m. p. 75—76° and m. p. 83—84°, which form two *anilides*, m. p. 178° and m. p. 143—145° respectively. Δ^3-cyclo*Citral*, $C_{10}H_{16}O$, obtained in a 60—70% yield from the anilide, m. p. 178°, is an oil, b. p. 53—54°/4 mm. or 76°/12 mm., and has a suffocating odour of carvone.

*a-cyclo*Geranic acid yields an anilide, m. p. 157—158°, from which a mixture of *a*- and *β-cyclo*citral is obtained in a 60—80% yield. Whilst

the conversion of *a-cyclo*geranic acid into the aldehyde is thus accompanied by a transmigration of the ethylene linking, *β-cyclo*geranic acid is converted by way of the *anilide*, m. p. 162°, into *β-cyclo*citral only.
G. Y.

Transformation of Carboxylic Acids into their Aldehydes. Hermann Staudinger (*Ber.*, 1908, 41, 2217—2219. Compare Merling, preceding abstract).—Carboxylic acids may be converted into their corresponding aldehydes as follows: the imide chloride is treated with magnesium, whereby a Grignard compound is formed; water decomposes the latter, yielding a Schiff's base, from which the aldehyde is obtained by treatment with dilute hydrochloric acid, thus:



$$R\cdot C\!<\!\begin{smallmatrix}NPh\\ Cl\end{smallmatrix} \longrightarrow R\cdot C\!<\!\begin{smallmatrix}NPh\\ MgCl\end{smallmatrix} \longrightarrow R\cdot C\!<\!\begin{smallmatrix}NPh\\ H\end{smallmatrix} \longrightarrow R\cdot CHO + NH_2Ph.$$

The reaction has been carried through with the imide chloride obtained from benzanilide. The imide chlorides derived from oxanilide and *iso*butyranilide react with magnesium, but the aldehydes have not been obtained.

The *imide chloride*, $CHMe_2\cdot CCl\colon NPh$, prepared by acting on *iso*butyranilide with phosphorus pentachloride, is a colourless liquid, b. p. 101—103°/13 mm., which decomposes slowly.

The *imide chloride*, $CHPh_2\cdot CCl\colon NPh$, derived from diphenylacetanilide, forms compact crystals, m. p. 94—95°. W. H. G.

Anisylidene Chloride. Hans Schmidt (*Ber.*, 1908, 41, 2331—2332. Compare Hoering and Baum, this vol., i, 527).—*Anisylidene chloride* is probably formed by the action of phosphorus pentachloride on anisaldehyde, but is best prepared by boiling 1 mol. of anisaldehyde with a little more than 1 mol. of thionyl chloride and about an equal volume of benzene for several hours under reflux, with exclusion of moisture. It has m. p. 20°, b. p. 130—132°/13 mm. 134°/14 mm., and is unstable. It is readily hydrolysed by cold water or alcoholic potash with formation of anisaldehyde. J. C. C.

Preparation of Aromatic Hydroxyaldehydes and Partially Alkylated Polyhydroxyaldehydes by Fission of the Corresponding Alkyl Derivatives. Camille Dreyfus (D.R.-P. 193958).—The well-known action of aluminium chloride on mixed ethers, such as phenetole, has been examined in the case of aromatic aldehydes containing alkoxyl groups, with the result that these substances have been converted into the corresponding hydroxyaldehydes.

Veratraldehyde, when dissolved in benzene or toluene and treated with re-sublimed aluminium chloride, furnishes a mixture of 3-dihydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, and *iso*vanillin.

Anisaldehyde, when similarly treated, yields *p*-hydroxybenzaldehyde.
G. T. M.

New Cyclic Ketones. Gustave Blanc (*Bull. Soc. chim.*, 1908, [iv], 3, 780—786).—These ketones were prepared by the process already given (Abstr., 1907, i, 710), namely, by heating the corresponding substituted adipic or pimelic acid with acetic anhydride and distilling the anhydride first formed. 1 : 1-Dimethyl*cyclo*pentan-5-one, b. p. 143°, prepared from αα-dimethyladipic acid (Abstr., 1906, i, 523), furnishes an *oxime*, m. p. 69°, which crystallises from light petroleum. When condensed with benzaldehyde in presence of alcohol and sodium hydroxide, the ketone gives 1 : 1-*dimethyl*-4-*benzylidene*cyclo*pentan*-5-*one*, m. p. 36°, which separates from light petroleum in bulky crystals. 1-*iso*Propyl*cyclo*pentan-5-one, obtained from *iso*propyladipic acid (Abstr., 1905, i, 681), yields a semicarbazone, m. p. 199—200° (compare Bouveault and Locquin, this vol., i, 173). 1 : 1-*Dimethyl*cyclo*pentan*-4-*one*, b. p. 153—154°, obtained from ββ-dimethyladipic acid, is a mobile liquid, and has an odour of camphor, benzaldehyde, and menthone; its *semicarbazone*, m. p. 178—179°, crystallises from methyl alcohol in colourless needles. 1 : 1-Dimethyl*cyclo*hexan-5-one, obtained from ββ-dimethylpimelic acid (compare Leser, Abstr., 1899, i, 743), gives a semicarbazone, m. p. 203°, which crystallises in colourless needles. The 2-(or 4-)*benzylidene* derivative of the ketone, m. p. 56°, separates from light petroleum in bulky, nearly colourless crystals. On reduction with sodium and alcohol, the ketone yields the corresponding hexanol (Crossley and Renouf, Trans., 1905, **87**, 1487).

1 : 1 : 4-Trimethyl*cyclo*hexane-5-onesemicarbazone (Abstr., 1907, i, 710) crystallises in colourless needles. T. A. H.

Products of Condensation of *o*- and *p*-Nitrobenzyl Chlorides with Acetylacetone. H. Mech (*Compt. rend.*, 1908, **146**, 1409—1411).—The author has prepared derivatives of δ-*p*-nitrophenyl-β-butanone and of di-*o*-nitrobenzylacetylacetone which he described recently (Abstr., 1907, i, 63).

δ-p-*Nitrophenyl-β-butanonesemicarbazone* is a white powder, m. p. 198·5°. When δ-*p*-nitrophenyl-β-butanone is reduced with zinc and hydrochloric acid, it yields δ-p-*aminophenyl-β-butanone* as a yellow mass, m. p. about 195° (decomp.). The *semicarbazone* forms colourless crystals, m. p. 153° (decomp.).

From the oil obtained along with di-*o*-nitrobenzylacetylacetone, it was not possible to isolate δ-*o*-nitrophenyl-β-butanone, but the *oxime*, m. p. 97°, and the *semicarbazone*, m. p. 169—170°, were prepared. J. C. C.

Preparation of ω-Nitroacetocatechol. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 195814).—When piperonaldehyde is treated successively with nitromethane, bromine, methyl-alcoholic potash, and acids, *ω-nitroacetopiperone*,

$$CH_2O_2{:}C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}NO_2,$$

is obtained, yellow leaflets or needles, m. p. 173°. *ω-Nitroacetoveratrone*, $C_6H_3(OMe)_2{\cdot}CO{\cdot}CH_2{\cdot}NO_2$, needles, m. p. 144°, is produced from veratraldehyde by a similar series of operations. These nitrated ketones, on treatment with aluminium chloride in benzene or toluene, lose their methylene and methyl groups respectively, and give rise to *ω-nitroacetocatechol*, $C_6H_3(OH)_2{\cdot}CO{\cdot}CH_2{\cdot}NO_2$, yellow crystals, blackening at 170—180°, and decomposing at 188°. On reduction, this compound furnishes aminoacetocatechol, which is of importance in connexion with the synthesis of bases of the adrenaline group. G. T. M.

Identity of Methysticol and Piperonyleneacetone. Erich Winzheimer (*Ber.*, 1908, 41, 2377—2883).—According to Pomeranz (Abstr., 1889, 278; 1890, 257), methysticol, a derivative of methysticin obtained from *Piper methysticum*, is identical with piperonyleneacetone, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}COMe$, synthesised by Scholtz (Abstr., 1895, i, 469). Pomeranz, however, states that methysticol has m. p. 94° and is readily soluble in alcohol and ether, whilst Scholtz's compound is described as having m. p. 89° and being only slightly soluble in these solvents. The present author, having obtained a quantity of methysticol in the course of other work, has prepared piperonyleneacetone, and on comparison finds the two substances to be identical, having m. p. 89·5—90° separately and when mixed. The phenylhydrazone has m. p. 152—152·5° (141°: Scholtz, *loc. cit.*); the *semicarbazone*, m. p. 199—199·5°; the *benzylidene* derivative, $C_{20}H_{16}O_3$, golden needles, m. p. 110—111°, forms a *phenylhydrazone*, crystallising in golden needles, m. p. 187·5—188°. The *piperonylidene* derivative, $C_{21}H_{16}O_5$, yellow needles, m. p. 195°.

Dipiperonyleneacetone (piperonylenemethysticol) has m. p. 203—204° (198—199°: Scholtz).

The following derivatives of piperonylacraldehyde were prepared; the m. p. in brackets are those given by Ladenburg and Scholtz (Abstr., 1895, i, 42) or by Scholtz and Kipke (Abstr., 1904, i, 508). The phenylhydrazone, m. p. 163—164° (160°); the semicarbazone, m. p. 234° (226°); *o*-toluidide, m. p. 92—92·5° (94—95°); *p*-toluidide, m. p. 139·5—140·5° (138°); acetophenone derivative, m. p. 137·5° (133°). G. Y.

Derivatives of Phenyl β-Naphthyl Ketone. Gustave Perrier and Caille (*Bull. Soc. chim.*, 1908, [iv], 3, 736—739).—Phenyl β-naphthyl ketone, regenerated from its additive product with aluminium chloride (Abstr., 1896, i, 353), furnishes (1) an *oxime*, m. p. 133°, which separates from alcohol in colourless, silky crystals and is insoluble in water, soluble in alcohol or toluene, and scarcely so in light petroleum; (2) a *phenylhydrazone*, m. p. 123°, which forms faintly yellow crystals from alcohol, reddens slightly on exposure to air, is paramagnetic, and gives a green coloration with sulphuric acid, and (3) a *semicarbazone*, m. p. 175°, which forms colourless crystals from alcohol. On reduction with sodium amalgam in alcohol at 60°, the ketone furnishes *phenylnaphthylcarbinol*, m. p. 83°, which crystallises from alcohol in colourless, silky needles and is diamagnetic; the *benzoyl* derivative, m. p. 110°, forms silky needles from alcohol and is diamagnetic. With the exception of the phenylhydrazone, all these derivatives, like the ketone, give red or orange-red colorations with sulphuric acid. T. A. H.

Preparation of 3 : 4-Dihydroxyphenylglyoxime and 3 : 4-Dihydroxyphenylalkylglyoximes. Chemische Fabrik auf Actien (vorm. E. Schering) (D.R.-P. 195655, 195656, 195657).—When treated with excess of hydroxylamine, preferably on warming, the 3 : 4-dihydroxyphenyl alkyl ketones of the type $C_6H_3(OH)_2\cdot CO\cdot CHXR$ (where X is hydrogen or alkyl and R a halogen) give rise to substituted glyoximes having the general formula $C_6H_3(OH)_2\cdot C(NOH)\cdot CX{:}NOH$. These products are of importance as the starting point in the preparation of bases having hæmostatic properties.

3 : 4-*Dihydroxyphenylglyoxime*, $C_6H_3(OH)_2\cdot C(NOH)\cdot CH{:}NOH$, white needles, m. p. 185—186°, is produced by warming ω-chloroacetocatechol with an aqueous solution containing hydroxylamine hydrochloride and sodium carbonate. This compound is also produced by the action of hydroxylamine on ω-aminoacetocatechol or dimethyl- or diethyl-ω-aminoacetocatechol. This reaction is especially remarkable, as it does not take place with aminoacetone or the dialkylaminoacetones.

This condensation occurs most readily in dilute acetic acid, and may also be effected with methyl-ω-aminoacetocatechol and piperidylacetocatechol.

4 : 4-*Dihydroxyphenylmethylglyoxime*,

$$C_6H_3(OH)_3\cdot C(NOH)\cdot CMe{:}NOH,$$

white needles, m. p. 201—202°. G. T. M.

Constitution of Some Derivatives of Diphenylmethane and Preparation of Some *o*-Diamino-compounds of the Same Series. Henri Duval (*Compt. rend.*, 1908, **146**, 1324—1326).—The constitution of acetyldiphenylmethane and dinitrodiphenylmethanedicarboxylic acid, described previously (this vol., i, 277), and of dinitrodiacetyldiphenylmethane is established.

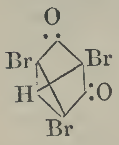
The first compound must be 4-acetyldiphenylmethane, since, on oxidation, it gives benzophenone-4-carboxylic acid. When 2 : 2′-dinitro-4 : 4′-diaminodiphenylmethane is converted through the diazo-reaction into the corresponding dinitrile and the latter hydrolysed, the 2 : 2′-dinitrodiphenylmethane-4 : 4′-dicarboxylic acid produced is identical with the acid formed by nitratng diphenylmethane-4 : 4′-dicarboxylic acid.

When 4 : 4′-diacetyldiphenylmethane is nitrated at − 10° with colourless nitric acid in the presence of sulphuric acid, 2 : 2′-*dinitro*-4 : 4′-*diacetyldiphenylmethane*, $CH_2(C_6H_3Ac\cdot NO_2)_2$, is formed in yellowish-white needles, m. p. 151°, which give an *oxime*, m. p. 224°. The position of the nitro-groups in this compound is fixed by the facts that on oxidation by sodium hypobromite and esterification of the resulting acid, the ester produced is identical with that formed by the oxidation of ethyl 2 : 2′-dinitrodiphenylmethane-4 : 4′-dicarboxylate, and that 2 : 2′-dinitrodiphenylmethane-4 : 4′-dicarboxylic acid is produced by the prolonged action of a mixture of nitric and sulphuric acids on 4 : 4′-diacetyldiphenylmethane. 2 : 2′-*Diamino*-4 : 4′-*diacetyldiphenylmethane* is formed by reducing the corresponding dinitro-derivative, and crystallises in yellow needles, m. p. 166°. When 2 : 2′-dinitro-4 : 4′-diaminodiphenylmethane is diazotised and treated with cuprous cyanide, 2 : 2′-*dinitro*-4 : 4′-*dicyanodiphenylmethane*,

$$CH_2[C_6H_3(NO_2)\cdot CN]_2,$$

bright yellow crystals, m. p. 195°, is formed. This on reduction gives 2 : 2′-*diamino*-4 : 4′-*dicyanodiphenylmethane*, yellow crystals, m. p. 236°. 2 : 2′-*Dinitro*-4 : 4′-*diacetyldiaminodiphenylmethane*, yellow crystals, m. p. 229°, is formed by the action of acetic anhydride on the amine, and when reduced gives 4 : 4′-*diacetyl*-2 : 4 : 2′ : 4′-*tetra-aminodiphenylmethane*, $CH_2[C_6H_3(NHAc)\cdot NH_2]_2$, white needles, m. p. 244°. E. H.

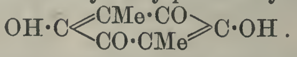
Tribromoresoquinone [*m*-Benzoquinone]. RICHARD MEYER and KURT DESAMARI (*Ber.*, 1908, **41**, 2437—2445).—Experiments are being made with the object of preparing simple meta-quinones. The present communication deals with the meta-quinone first described by Leibermann and Dittler (Journ., 1872, 297), namely, tribromoresoquinone. This compound has been carefully analysed and its mol.-wt. determined; the results obtained show definitely that the compound has the molecular formula $C_6HO_2Br_3$, and not the bimolecular formula proposed by Benedikt (Abstr., 1879, 55, 464, 717), and that its chemical properties are best represented by the annexed formula. Tribromoresoquinone possesses the characteristic properties of quinones; thus it liberates iodine from potassium iodide.



It is reduced when treated with hydroxylamine and phenylhydrazine, yielding tetrabromodiresorcinol (compare Benedikt, *loc. cit.*). The results of mol.-wt. determinations agree with the formula $C_{12}H_6O_4Br_4$ assigned by Benedikt to this compound.

W. H. G.

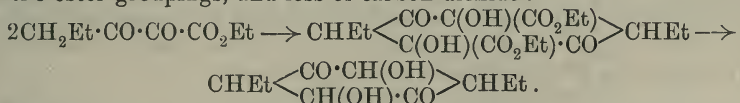
Synthetical *p*-Dialkylated Dihydroxyquinones. FRITZ FICHTER (*Annalen*, 1908, **361**, 363—402).—It was shown previously (Fichter and Willmann, Abstr., 1904, i, 678) that certain red, crystalline by-products, obtained when metallic sodium is used instead of sodium ethoxide as the condensing agent in the synthesis of ethyl alkyloxalacetates from ethyl oxalate and esters of monobasic fatty acids, are dihydroxyquinones derived from *p*-dialkylbenzenes. Thus ethyl oxalate and ethyl propionate yield dihydroxy-*p*-dimethylbenzoquinone,



$$OH\cdot C{<}{\substack{CMe\cdot CO\\ CO\cdot CMe}}{>}C\cdot OH\,.$$

The mechanism of the synthesis has now been studied, and a number of derivatives and hydrolysis products of dihydroxy-*p*-dialkylbenzoquinones are described.

The dihydroxy-*p*-dialkylbenzoquinones cannot be formed by way of the ethyl alkyloxalacetates, since they are obtained only when sodium is employed as condensing agent, whereas the ethyl alkyloxalacetate formation takes place most easily with sodium ethoxide; on the other hand, ethyl oxalate and ethyl acetate do not form a dihydroxybenzoquinone even with sodium. Moreover, whilst the formation of ethyl alkyloxalacetates takes place only with ethyl propionate and ethyl butryate, and not with ethyl *iso*valerate, dihydroxybenzoquinones are formed, not only from these three esters, but also from ethyl *n*-hexoate, *n*-heptoate, phenylacetate, and hydrocinnamate. According to Claisen's view of the action of sodium on ethyl *iso*butyrate (Abstr., 1897, i, 592), the first product of the condensation of ethyl oxalate and ethyl butyrate by means of sodium must be an $\alpha\beta$-diketonic ester, formed according to the scheme: $CH_2Et\cdot CO_2Et + C_2O_4Et_2 + Na_2 = CH_2Et\cdot CO\cdot CO\cdot CO_2Et + 2NaOEt$. In agreement with this, it is found that the yield of dihydroxyquinone is greater when 1 mol. than when 1 atom of sodium is employed for the condensation of 1 mol. of ethyl oxalate with 1 mol. of ethyl butyrate, whereas 1 atom of sodium suffices for the oxalacetate synthesis with the same amount of two esters. It is considered that the synthesis under discussion takes place by way of the $\alpha\beta$-diketonic ester, which undergoes ring condensation, hydrolysis of the ester groupings, and loss of carbon dioxide:



$$\mathrm{2CH_2Et\cdot CO\cdot CO\cdot CO_2Et} \longrightarrow \mathrm{CHEt}{<}\begin{matrix}\mathrm{CO\cdot C(OH)(CO_2Et)}\\ \mathrm{C(OH)(CO_2Et)\cdot CO}\end{matrix}{>}\mathrm{CHEt} \longrightarrow \mathrm{CHEt}{<}\begin{matrix}\mathrm{CO\cdot CH(OH)}\\ \mathrm{CH(OH)\cdot CO}\end{matrix}{>}\mathrm{CHEt}.$$

1. *Synthesis of Dihydroxy*-p-*dialkylbenzoquinones.*—[With EUGEN WEISS.]—The following derivatives of dihydroxy-*p*-dialkylbenzoquinones, previously described, have now been prepared.

Dihydroxy-p-*xyloquinone diacetate*, $C_{12}H_{12}O_6$, crystallises in yellow needles, m. p. 146·5°, and on reduction with zinc dust and glacial acetic acid yields *tetra-acetoxy*-p-*xylene*, $C_{12}H_{14}O_6$, crystallising in white needles, m. p. 242°.

Dihydroxy-p-*diïsopropylbenzoquinone dibenzoate*, $C_{26}H_{24}O_6$, crystallises in yellow needles, m. p. 220°.

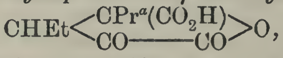
Dihydroxy-p-*di*-n-*butylbenzoquinone*, $C_{14}H_{20}O_4$, prepared from ethyl oxalate and ethyl *n*-hexoate, separates from glacial acetic acid in red crystals, m. p. 175° in a sealed capillary tube, forms in aqueous alkalis a violet, in concentrated sulphuric acid a dark blue, solution, and when boiled with aqueous sodium hydroxide undergoes the succinic acid hydrolysis. The *diacetate*, $C_{18}H_{24}O_6$, forms yellow needles, m. p. 60°.

Dihydroxy-p-*diphenylbenzoquinone*, $C_{18}H_{12}O_4$, prepared from ethyl phenylacetate and ethyl oxalate, forms violet-brown crystals, decomp. 280—300°, gives with aqueous alkalis a violet, with concentrated sulphuric acid a brown, coloration, and dyes mordants more feebly than the dialkyl compounds.

Dihydroxy-p-*dibenzylbenzoquinone*, $C_{20}H_{16}O_4$, prepared from ethyl hydrocinnamate and ethyl oxalate, crystallises in red leaflets, m. p. 225° in a sealed tube, gives colorations similar to those of the preceding substance, and is a strong dye. The *diacetate*, $C_{24}H_{20}O_6$, forms yellow needles, m. p. 182°.

2. *Synthesis of Dihydroxy*-p-*dialkylquinones.*—[With MAX JETZER.]—Comparative experiments on the influence of different solvents and of different alkyl groups on the formation of dihydroxy-*p*-dialkylbenzoquinones show that better yields are obtained in benzene or toluene than in ethereal solution, that methyl oxalate and methyl butyrate give better yields than the ethyl or *iso*amyl esters, and that ethyl oxalate condensed with methyl *iso*valerate gives a better yield of the dihydroxybenzoquinone than a mixture of the methyl esters, a mixture of the ethyl esters, or a mixture of methyl oxalate with ethyl *iso*valerate. The reaction takes place more easily with the *iso*valerate than with the butyrate.

3. *Hydrolysis of Dihydroxy-*p*-dixyloquinone and Dihydroxy-*p*-diethylbenzoquinones.*—[With Hans Kappeler.]—When boiled with sodium hydroxide in aqueous solution, dihydroxy-p-xyloquinone yields *s*-methylethylsuccinic acid, m. p. 178°, and *as*-methylethylsuccinic acid, m. p. 99—-100°. These two acids are obtained also by the hydrolysis of α-keto-β-methylhexolactone-γ-carboxylic acid (Fichter and Preiswerk, Abstr., 1902, i, 443) by means of boiling 5% sodium hydroxide. The hydrolysis of dihydroxy-*p*-diethylbenzoquinone in the same manner leads to the formation of s-*ethylpropylsuccinic acid*, $C_9H_{16}O_4$, m. p. 174—175°, which forms a *barium* salt, $C_9H_{14}O_4Ba,H_2O$, and an *ethyl* ester, $C_{13}H_{24}O_4$, colourless oil, b. p. 134—135°/16 mm., and as-*ethylpropylsuccinic acid*, which crystallises in stellate aggregates, m. p. 97—98°. These ethylpropylsuccinic acids are obtained also by hydrolysis of *α-keto-β-ethylheptolactone-γ-carboxylic acid*,



$$\mathrm{CHEt}<\begin{matrix}\mathrm{CPr^{a}(CO_2H)}\\ \mathrm{CO}\text{———}\mathrm{CO}\end{matrix}>\mathrm{O},$$

which is formed by heating butyrylformic acid with 75% sulphuric acid, crystallises in colourless needles, m. p. 110—111°, and gives an intense red coloration with ferric chloride.

4. *Hydrolysis of Dihydroxy-*p*-di*iso*propylbenzoquinone and Dihydroxythymoquinone.*—[With Heinrich Glaser.]—The hydrolysis of dihydroxy-*p*-di*iso*propylbenzoquinone with boiling dilute sodium hydroxide leads to the formation of two iso*propyl*iso*butylsuccinic acids*, which are not identical with Beatty's acids (Abstr., 1903, i, 726).

*iso*Propyl*iso*butylsuccinic acid, $C_{11}H_{20}O_4$, m. p. 185—186°, crystallises from hot water in colourless needles, or from cold water separates in crystals containing H_2O. The *calcium* salt,

$$C_{11}H_{18}O_4Ca,H_2O,$$

is colourless. The *anhydride*, $C_{11}H_{18}O_3$, formed by boiling the acid with acetic anhydride, is obtained as a colourless oil, b. p. 150°/12 mm., and when boiled with water yields the acid, m. p. 185—186°.

*iso*Propyl*iso*butylsuccinic acid, m. p. 124°, crystallises from water in cubes, is volatile with steam, and can by extracted from the aqueous distillate by ether. The *barium*, $C_{11}H_{18}O_4Ba,2H_2O$, and *calcium*,

$$C_{11}H_{18}O_4Ca,2H_2O,$$

salts were analysed. The *anhydride* is formed when the anhydride of the acid of higher m. p. is distilled under the ordinary pressure; it is a slightly yellow liquid, b. p. 264—265°, and when boiled with water yields the acid, m. p. 124°. When heated with 18% hydrochloric acid at 180—220°, the acid, m. p. 124, is converted into the acid, m. p. 185—186°.

Diethyldiaminothymoquinone, $C_{14}H_{22}O_2N_2$, prepared from ethylamine, forms violet-red needles, m. p. 116°.

On hydrolysis with sodium hydroxide, dihydroxythymoquinone yields two *ethyl*iso*propylsuccinic acids*, $C_9H_{16}O_4$. Ethyl*iso*propylsuccinic acid, m. p. 210°, crystallises from water in colourless needles, and forms a *calcium* salt, $C_9H_{14}O_4Ca,H_2O$. This acid can be prepared also by condensation of ethyl ethylmalonate with ethyl α-bromo*iso*valerate by means of sodium; the intermediate *ethyl tricarboxylate*,

$$C_{16}H_{20}O_6,$$

has b. p. 164°/12 mm.

Ethyl*iso*propylsuccinic acid, m. p. 96°, crystallises in cubes; the *calcium* salt, $C_9H_{14}O_4Ca,H_2O$, forms long needles.

Dihydroxytoluquinones are best prepared by the action of methylamine on toluquinone and hydrolysis of the tetra-acetate of this, when the resulting tetrahydroxytoluene is rapidly oxidised by air to the dihydroxytoluquinone.

Di-p-*methylaminotoluquinone*, $NHMe\cdot C_6HO_2Me\cdot NHMe$, forms a brown, crystalline powder, m. p. 235°. The *tetra-acetate*,

$$C_6HMe(OAc)_4,$$

crystallises in needles, m. p. 198°. This tetra-acetate differs from the dialkylated compounds in that its alkaline solution does not become colourless even on prolonged boiling; the product is a black, syrupy mass, from which a crystalline acid could not be isolated. G. Y.

Preparation of αβ-Dihydroxyanthraquinones and αβ-Hydroxyanthraquinonesulphonic Acids. R. WEDEKIND & Co. (D.R.-P. 195874).—The 1 : 6- and 1 : 7-anthraquinonesulphonic acids when heated under pressure with water, calcium hydroxide, potassium nitrate, and calcium chloride yield a mixture of 1 : 6- and 1 : 7-dihydroxyanthraquinones and an intermediate hydroxyanthraquinonesulphonic acid. G. T. M.

Preparation of Halogen Derivatives of Benzanthrone, BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 193959. Compare Abstr., 1907, i, 324).—A *bromobenzanthrone*, yellow needles or leaflets, m. p. 170°, is obtained by brominating benzanthrone in acetic acid solution. Chlorination of benzanthrone in the same medium leads to the formation of two dichlorobenzanthrones, which are separated by fractional crystallisation from acetic anhydride, glacial acetic acid, or nitrobenzene; these isomerides crystallise in yellow needles, and melt respectively at 269° and 218°. By chlorinating benzanthrone with potassium chlorate and hydrochloric acid in 50% acetic acid, a *chlorobenzanthrone* is obtained, golden-yellow needles m. p. 176°. *Bromobenzanthronequinoline,* golden-yellow needles, m. p. 298°, is produced by brominating benzanthronequinoline. These products differ from those obtained by condensing the halogenated anthraquinones with glycerol in containing the halogen in the anthrone ring. On oxidation, they furnish anthraquinone-1-carboxylic acid, whereas the former series give rise to the halogen derivatives of this acid. G. T. M.

Direct Transformation of Borneol into Campholic and *iso*Campholic Acids. MARCEL GUERBET (*Compt. rend.*, 1908, **147**, 70—72. Compare Abstr., 1901, i, 307.)—When borneol is heated at 250—280° in sealed tubes with recently-fused potassium hydroxide, it is almost completely transformed into a mixture of potassium campholate and *iso*campholate, thus:

$$C_{10}H_{18}O + KOH = C_{10}H_{17}O_2K + H_2.$$

This is probably to be explained by the rupture of one of the rings in borneol in two different ways, one giving campholic, and the other *iso*campholic, acid. The two acids are readily separated, since the former is precipitated from its alkaline solutions by carbon dioxide, and, moreover, it is not esterified by hydrochloric acid and alcohol.

The campholic acid obtained has $\alpha + 46 \cdot 6°$, differing somewhat from the value $+49 \cdot 8°$ obtained by Montgolfier (Abstr., 1878, 891). From 36 grams of borneol, 26·5 grams of crude campholic acid, 1·10 grams of *iso*campholic acid, 3·30 grams of borneol, and some neutral oily products are obtained. E. H.

Compounds of the Citronella Series. Carl D. Harries and Alfred Himmelmann (*Ber.*, 1908, 41, 2187—2199. Compare this vol., i, 714).—An investigation of the ozonides of citronellaldehyde, citronellol, and citronellic acid. These compounds decompose when treated with water, yielding acetone and β-methyladipic acid, except in the case of the ozonide of citronellol, when acetone, but not β-methyladipic acid, is obtained. The quantities obtained are 21, 32, and 52% of acetone, and 0, 35, and 58% of β-methyladipic acid respectively.

The quantities of acetone obtained closely correspond with those of β-methyladipinic acid. From these results, the authors consider it highly probable that compounds of the citronella series which have hitherto been regarded as simple substances are mixtures of compounds of the citronella series, $CH_2{:}CMe \cdot [CH_2]_3 \cdot CHMe \cdot CH_2R$, with those of the isomeric rhodina series, $CMe_2{:}CH \cdot [CH_2]_2 \cdot CHMe \cdot CH_2R$. For example, ordinary citronellaldehyde is probably a mixture of a compound having the formula assigned by Barbier (Abstr., 1897, i, 537) and Harries (Abstr., 1901, i, 730) to citronellaldehyde, namely, $CH_2{:}CMe \cdot [CH_2]_3 \cdot CHMe \cdot CH_2 \cdot CHO$, with a substance having the constitution assigned by Bouveault (Abstr., 1900, i, 452) to the aldehyde derived from rhodinol, namely,

$$CMe_2{:}CH \cdot [CH_2]_2 \cdot CHMe \cdot CH_2 \cdot CHO\ ;$$

the latter formula was originally given by Tiemann and Schmidt to citronellaldehyde (Abstr., 1897, i, 198). From the quantities of acetone obtained from the various ozonides, it follows that ordinary citronellol contains about 20% of rhodinol, citronellaldehyde about 40% of rhodinaldehyde, whilst citronellic acid contains about 60% of rhodinic acid.

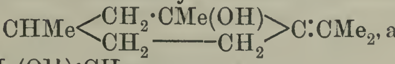
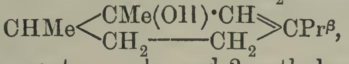
The ketonic substances which would result from the ozonides of the citronella series ($CH_2{:}CMe \cdot CH_2 \ldots$) on treatment with water, namely, $X \cdot CH_2 \cdot OH$ from citronellol, $X \cdot CHO$ from citronellaldehyde, and $X \cdot CO_2H$ from citronellic acid, where $X = Me \cdot CO \cdot [CH_2]_3 \cdot CHMe \cdot CH_2-$, were not isolated.

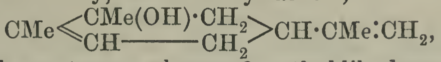
This assumption explains why Tiemann and Schmidt (*loc. cit.*) obtained only 50% of *iso*pulegol on treating the aldehyde with acetic anhydride, and why only one-half of the citronellaldimethylacetal when oxidised with potassium permanganate is converted into the dimethylsemiacetal of β-methyladipic acid (Harries and Schauwecker, Abstr., 1901, i, 448).

The compound obtained by acting on citronellaldehyde with ozone is an *ozonide peroxide*, $C_{10}H_{18}O_5$ (compare Langheld, Abstr., 1906, i, 226); it is converted by sodium hydrogen carbonate solution into the normal *ozonide*, $C_{10}H_{18}O_4$. The *ozonide*, $C_{10}H_{18}O_6$, obtained by passing ozone into a solution of the aldehyde in carbon tetrachloride, is a non-explosive, colourless, syrupy liquid with an unpleasant odour.

An *ozonide peroxide* of citronellic acid, $C_{10}H_{18}O_6$, is formed when ozone is passed into a solution of the acid in carbon tetrachloride until the solution no longer decolorises a solution of bromine in acetic acid. It is a slightly explosive, colourless, viscid liquid, which, when treated with water, yields an *ozonide*, $C_{10}H_{18}O_5$. An *ozonide*, $C_{10}H_{18}O_7$, is obtained by passing ozone into the solution in carbon tetrachloride until the latter becomes blue; it is similar in properties to the ozonide peroxide. An *ozonide* of citronellol, $C_{10}H_{20}O_6$, is obtained by passing ozone into a solution of citronellol in carbon tetrachloride; it is a non-explosive, colourless, viscid liquid.

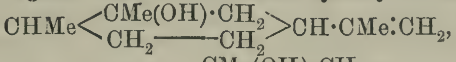
W. H. G.

A Hydrocarbon from *iso*Pulegone. HANS RUPE and A. EBERT (*Ber.*, 1908, 41, 2067—2071).—The action of magnesium methyl iodide on *iso*pulegone leads to the formation of a tertiary alcohol which loses water with moderate ease. It has been found previously (Abstr., 1906, i, 374; this vol., i, 433, 556) that the stability of tertiary alcohols of this series depends on the relative position in the molecule of the carbinol group and an ethylene linking, the loss of water taking place the more readily the nearer these are together. Thus 3-methylpulegol,  $CHMe<\begin{array}{l}CH_2\cdot CMe(OH)\\CH_2\text{———}CH_2\end{array}>C{:}CMe_2$, and 2-methylcarvenol,  $CHMe<\begin{array}{l}CMe(OH)\cdot CH\\CH_2\text{———}CH_2\end{array}>CPr^{\beta}$, cannot be isolated, as they lose water spontaneously, and 2-methylcarveol,

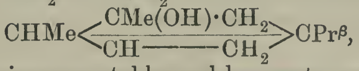
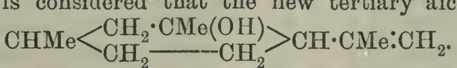
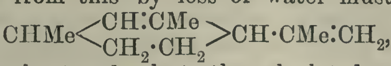


$$CMe\leqslant\begin{array}{l}CMe(OH)\cdot CH_2\\CH\text{———}CH_2\end{array}>CH\cdot CMe{:}CH_2,$$

loses water with great ease, whereas 2-methyldihydrocarveol,



$$CHMe<\begin{array}{l}CMe(OH)\cdot CH_2\\CH_2\text{———}CH_2\end{array}>CH\cdot CMe{:}CH_2,$$

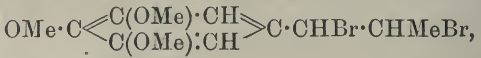
and homothujyl alcohol,  $CHMe<\begin{array}{l}CMe(OH)\cdot CH_2\\CH\text{———}CH_2\end{array}>CPr^{\beta}$, which does not contain an ethylene linking, are stable, and lose water only with great difficulty. Hence it is considered that the new tertiary alcohol is 3-*methyl*iso*pulegol*,  $CHMe<\begin{array}{l}CH_2\cdot CMe(OH)\\CH_2\text{———}CH_2\end{array}>CH\cdot CMe{:}CH_2$. The hydrocarbon formed from this by loss of water must be 3-*methyl*-$\Delta^{2,8(9)}$-*menthadiene*,  $CHMe<\begin{array}{l}CH{:}CMe\\CH_2\cdot CH_2\end{array}>CH\cdot CMe{:}CH_2$, as the molecular refraction approximates closely to the calculated, which excludes the possibility of the presence of conjugated ethylene linkings. The substances described may, however, be mixtures of isomerides (compare Wallach, this vol., i, 402).

3-Methyl*iso*pulegol, $C_{11}H_{20}O$, is a mobile oil, b. p. 93—94°/12 mm., D^{20} 0·9108, n_D 1·4699, $[\alpha]_D^{20}$ 19·54°, has an odour resembling geraniol, and, on treatment with phosphorus trichloride in ethereal solution, yields 3-*chloro*-3-*methyl*-$\Delta^{8(9)}$-*menthene*, $C_{11}H_{19}Cl$, which is obtained as a mobile, colourless oil, b. p. 92—93°/10 mm., gradually decomposing at the ordinary temperature.

3-Methyl-$\Delta^{2,8(9)}$-menthadiene, $C_{11}H_{18}$, prepared by heating the preceding chloro-compound with potassium acetate in alcoholic solution, or by converting the tertiary alcohol into its *acetyl* derivative and distilling this under the ordinary pressure and again over sodium, forms a mobile liquid having a slight odour of menthene. Of the following physical constants, the first series is those obtained with the hydrocarbon prepared from the chloro-compound, and the second with that from the acetyl derivative, b. p. 180—185°/750 mm. or 95—97°/12 mm., D^{20} 0·8401, n_D^{20} 1·4734, $[\alpha]_D^{20}$ +29·00°; b. p. 182—184°/750 mm. or 95—97°/12 mm., D^{20} 0·8400, n_D^{20} 1·4724, $[\alpha]_D^{20}$ +46·27°.

G. Y.

Components of Ethereal Oils. Establishment of the Constitutional Formulæ of Elemicin and *iso*Elemicin. Friedrich W. Semmler (*Ber.*, 1908, **41**, 2183—2187).—Elemicin (compare this vol., i, 557) is definitely shown to be 3 : 4 : 5-trimethoxy-1-allylbenzene; *iso*elemicin is therefore 3 : 4 : 5-trimethoxy-1-propenylbenzene. Elemicin, obtained by fractional distillation from the ethereal oil, has been further purified by treatment with concentrated formic acid; it then has b. p. 144—147°/10 mm., D^{20} 1·063, n_D 1·52848. *iso*Elemicin, obtained from elemicin purified in this manner, has b. p. 153—156°/10 mm., D^{20} 1·073, n_D 1·54679. It is converted by bromine dissolved in carbon tetrachloride into iso*elemicin dibromide*,



$$\mathrm{OMe\cdot C}\!\left\langle\begin{matrix}\mathrm{C(OMe)\cdot CH}\\ \mathrm{C(OMe)\colon CH}\end{matrix}\right\rangle\!\mathrm{C\cdot CHBr\cdot CHMeBr},$$

forming crystals, m. p. 89—90°.

W. H. G.

Preparation of Santalyl Camphorate. J. D. Riedel (D.R.-P. 193960).—*Santalyl camphorate*, yellow oil, D 0·9945/24°, is produced by heating methyl camphorate with 2 to 4 parts of santalol, or the corresponding amount of sandal-wood oil at 150—200° for several hours. The excess of santalol, or oil, is expelled in steam, and the new ester is obtained from the residue.

G. T. M.

Reduction of Aliphatic Terpene Compounds. C. J. Enklaar (*Ber.*, 1908, **41**, 2083—2087).—$\beta\zeta$-Dimethyloctane (Willstätter and Mayer, this vol., i, 383) is obtained by reduction of ocimene (van Romburgh, Abstr., 1901, i, 220), geraniol, or linalool with hydrogen in presence of nickel at 130°. When reduced with sodium and alcohol, and thereafter treated with bromine, ocimene and myrcene yield the same *dihydro-ocimene tetrabromide*, m. p. 88°. Hence ocimene, *allo*-ocimene, and myrcene are derivatives of the same decane. A comparison of the properties of $\beta\zeta$-dimethyloctane obtained with those of Willstätter and Mayer's preparation shows that, whilst ocimene does not contain cyclic terpenes, myrcene cannot be freed from these.

Reduction of geraniol with limited amounts of hydrogen leads to the formation of decanol (Willstätter and Mayer, *loc. cit.*), together with a cyclic *alcohol*, $C_{10}H_{20}O$, D_4^{15} 0·906, which yields a *phthalate*, m. p. 169—170°, and is therefore not identical with *r*-menthol or thymomenthol, and considerable amounts of a *product*, $C_{31}H_{57}O$, b. p. 192—194°/22 mm., D_4^{15} 0·8500, n_D^{19} 1·4564.

G. Y.

Phellandrene from Water Fennel Oil. IWAN L. KONDAKOFF (*J. pr. Chem.*, 1908, [ii], 78, 42—46).—It has been shown previously that the so-called natural phellandrene, obtained from water fennel oil, consists of a mixture of a phellandrene and at least 20% of pinene, which, on treatment with hydrogen chloride, forms *d*-bornyl chloride, dipentene dihydrochloride, and a mixture of liquid hydrochlorides. These when treated with alcoholic potassium hydroxide yield Kindt's camphor and a hydrocarbon containing small amounts of dipentene (Abstr., 1907, i, 329, 712, 713). These various products have now been further investigated. It is found that, on treatment with hydrogen chloride in various solvents, natural phellandrene yields *d*-bornyl chloride, with or without small amounts of dipentene dihydrochloride, formed from pinene, and an unsaturated monohydrochloride, sometimes together with a stable, liquid dihydrochloride, formed from the phellandrene. An optically inactive hydrocarbon, b. p. 177—182°, D^{15} 0·848, n_D 1·47877, containing possibly traces of camphene and dipentene, is obtained from the monohydrochloride and from the stable dihydrochloride. This hydrocarbon resinifies rapidly on exposure to air, and forms a liquid nitrite, liquid bromide, and liquid dihydrochloride. As the hydrochlorides of pinene have smaller rotatory powers than the hydrocarbon, and as natural phellandrene yields bornyl chloride with $[\alpha]_D^{17\cdot5} + 28\cdot3°$, the pinene contained in natural phellandrene must have a rotatory power not less than 35°, whilst the hydrocarbon, ψ- or β-phellandrene, must boil above 173°, have a density less than 0·858, and be optically inactive. The constitutions of α- and β-phellandrene remain to be determined.

G. Y.

Ethereal Oils. HEINRICH HAENSEL (*Chem. Zentr.*, 1908, i, 1837; from *Geschäftsber*, October, 1907, March, 1908).—*Acaroid resin oil* is reddish-brown in colour, and in odour resembles tolu- and peru-balsam, D^{20} 0·9600, $\alpha_D \pm 0°$, acid number 4·7, ester number 37·5. *Birch-leaf oil*, yellow in colour and solid at the ordinary temperature, D^{80} 0·8683, acid number 30, ester number 81, and from which a paraffin was obtained crystallising in leaflets, m. p. 49—50°. *Coriander oil* free from terpene has D^{15} 0·8786, $\alpha_D + 9\cdot5°$, ester number 13·3. *Oil of Cubebs*, obtained from cubeben, D 0·941, $\alpha_D - 13\cdot55°$. *Guaiacum resin oil* is a dark brown, aromatic-smelling oil, which is not completely soluble in 96% alcohol, D^{15} 0·9417, acid number 77, ester number 13·8, and when warmed with ammoniacal silver solution gives a silver mirror. *Rock-rose oil*, obtained from the dried plant, is dark brown and has an unpleasant odour, D^{21} 0·9296, acid number 0, ester number 111; it contains neither aldehyde nor ketone. *Laurel-leaf oil* has D 0·9361, $\alpha_D - 15\cdot95°$, and, besides *l*-pinene, probably contains some phellandrene. *Celandine oil*, from the dry plant, is brown and has a pleasant odour; it solidifies at 30°, and has D^{40} 0·9374. *Oil of Frankincense*, $D^{17\cdot5}$ 0·8810, $\alpha_D + 22\cdot08°$, acid number 2, ester number 15·5, contains an alcohol, $C_{26}H_{44}O$. *Olibanol*, which is a thick, yellow oil, b. p. 205—212°, D^{20} 0·9570, $\alpha_D - 65\cdot05°$.

J. V. E.

Ethereal Oils. SCHIMMEL & Co. (*Chem. Zentr.*, 1908, i, 1838—1840; from *Geschäftsber*, April 1908. Compare Abstr., 1907, i, 782—783).—Ayapana oil has D^{15} 0·9806, α_D +2·92°, acid number 5·5, ester number 5·9; the yield of this oil from the leaves of *Eupatorium triplinerva* from Ceylon, 1·14%. A fraction obtained from camphor oil, b. p. 175·5—177°/763 mm., D^{15} 0·8470, α_D +39·77°, contained a considerable quantity of *d*-limonene with dipentene. Oil of lemon from Java may occasionally be dextrorotatory up to +1·77°; an oil not differing in properties from Java oil of lemon had D^{15} 0·9058, α_D +0·17°, a total content of 79·7% ($C_{10}H_{18}O$), and was soluble in 1 vol. 80% alcohol. Oil of bergamot from Ischia Island does not differ from the ordinary commercial oil from Messina; it is brownish-green in colour and strong smelling, D^{15} 0·8828, α_D +13°, acid number 1·8, ester number 96·4, and corresponds with 33·7% linalyl acetate; non-volatile residue, 5·2%. A small quantity of oil (yield, 2·94%) distilled from the seeds of *Heracleum giganteum* had the following constants: D^{15} 0·8738, α_D + 1°, n_D^{20} 1·42402, acid number 3·7, ester number 281·9, after acetylation 311·8, and dissolved in 1·2 vols. 80% alcohol. Kobuschi oil from the young twigs and leaves of *Magnolia Kobus* had D^{15} 0·9451, α_D −1·5°, acid number 0·7, ester number 4·3, and contained citral and cineol together with about 16% anethole and probably also methylchavicol.

Oil from *Lavandula stoechas* contains *d*-fenchone and *d*-camphor. A sample of *Niaouli oil* (from *Melaleuca viridiflora*) obtained from New Caledonia was pale lemon-yellow in colour, smelling strongly like eucalyptol, and had D^{15} 0·9284, α_D −1·17°; it contained about 40% cineol. Oil of Savin does not contain pinene, thus enabling any adulteration with turpentine oil to be detected.

Canadian Snakeroot oil, from the air-dried disintegrated root of *Asarum canadense* (Indian ginger root, wild ginger), yields 3·36% of a yellowish-brown aromatic oil, D^{15} 0·9508, α_D −22°, n_D^{20} 1·48537, acid number 3·7, ester number 115·9, after acetylation 140·1, soluble in 2·7 vols. and more of 70% alcohol. The oil obtained from the root without the fibre (yield, 3·83%) is purer yellow in colour, and has D^{15} 0·9516, α_D −2·83°, n_D^{20} 1·48508, acid number 3·7, ester number 117·6, after acetylation 137·2, and it dissolves in 2·3 vols. 70% alcohol. The oil from the fibre of the root (yield, 1·20%) had D^{15} 0·9659, α_D −39·66°, n_D^{20} 1·50280, acid number 2·2, ester number 39·2, after acetylation 110·2, and is not soluble in 10 vols. 70% alcohol, but soluble in 0·9 vols. 80% alcohol.

The residue obtained from the purification of American turpentine oil gives, when fractionated, portions which are rich in β-pinene, especially the fraction, b. p. 164—166°.

American Wormseed oil (from *Chinopodium ambrosioïdes* var. *anthelminticum*) has D 0·96—0·98, and dissolves in 10 vols. 70% alcohol to a clear solution; oils have, however, for some time been met with having D 0·93—0·95, which are only soluble in 80% alcohol, the difference in properties being caused by a slow distillation process. It is advised to distil at a moderate rate and to employ only the seeds of the plant; the plant free from seeds gives no oil. A careful investigation of this oil showed D^{15} 0·9768, α_D −4·5°, n_D^{20} 1·47850, acid number

0, saponification number 8·4, after acetylation 280·1, and it was soluble in 4 vols. 70% alcohol. The acetylated oil was heavier than water, and had a strong scent similar to spearmint. Small quantities of a terpene, probably silvestrene, *p*-cymene, and also *d*-camphor have been found in the oil; the chief constituent, however, is a repugnant-smelling substance, *ascaridol*, $C_{10}H_{16}O_2$, b. p. 83°/4—5 mm., D^{15} 1·0079, $\alpha_D - 4·25°$, n_D^{20} 1·47431. Towards reagents which show alcoholic, aldehydic, ketonic, or phenolic characters, this substance is quite indifferent only with 50% resorcinol solution does it give, at the ordinary temperature, an unstable liquid compound, which when heated to 130—150° decomposes with explosive violence. It appears that at 150° a transformation takes place; the product purified by vacuum distillation had b. p. 98·5—99·5°/4·5 mm., D^{15} 1·0266, $\alpha_D \pm 0°$, n_D^{20} 1·46545, and had a similar composition to that given above. Ascaridol reacts violently with concentrated formic acid, giving cymene, but less readily with alcohol, potassium hydroxide, or zinc chloride; zinc dust and acetic acid give cymene and probably also carvenone. Oxidation with potassium permanganate (1% solution) gives an acid mixture in which, besides formic, acetic, and *iso*butyric acids, a higher boiling liquid acid is obtained ($C_{10}H_{16}O_4$), b. p. 80—81°/5 mm., D^{15} 1·0641, $\alpha_D \pm 0°$, n_D^{20} 1·44388, which when heated to 120—130° gives methylheptenone. The transformation product of ascaridol decomposes when boiled with water, and gives with zinc dust and acetic or formic acid no cymene, but with the latter a ketone, $C_8H_{14}O$, semicarbazone, m. p. 194—195°. Normal American oil (D^{15} 0·9708) contains 62—65% of ascaridol and about 22% of cymene, but light oil (D^{15} 0·9426), only 45—50% of ascaridol.

Hyssop oil, from dried flowering plants, had D^{15} 0·9377, $\alpha_D - 22·5°$, acid number 1·8, ester number 5·8, after acetylation 44, and is soluble in about 6 vols. 80% alcohol with separation of paraffin. From withered flowering plants, the oil had D^{15} 0·9322, $\alpha_D - 22·4°$, acid number 1·3, ester number 3·6, after acetylation 37·3, n_D^{20} 1·48315, and is soluble in about 8 vols. 80% alcohol with separation of paraffin. Very faded flowering plants yielded an oil, D^{15} 0·9336, $\alpha_D - 20·43°$, n_D^{20} 1·48441, acid number 1·8, ester number 3·1, and is soluble in about 7 vols. 80% alcohol with separation of paraffin; the last oil appears to contain β-pinene, *l*-pinocamphone, and a very small quantity of an alcohol, b. p. 221—222°. The higher boiling portions of this oil are probably sesquiterpenes. A beautiful crystalline *dibromide* has been obtained from *l*-pinocamphone, m. p. 93—94°, which gives in alcohol solutions an alcohol of camphor-like odour, m. p. 67—68°, b. p. 217—218°. When reduced or oxidised, it yields l-*pinonic acid*, $C_{10}H_{16}O_3$, m. p. 69·5—70·5°, but when oxidised by sulphuric acid, l-*menthoethylheptanonolide*, m. p. 46—47°, is produced.

The following oils from Mayotte are described for the first time: Two *Basilicum oils*, one of which contains eugenole, whilst the other, from *B. canum* (*Ocimum canum*), contains a considerable quantity of *d*-camphor; also an oil from Mexico from the leaves of *Schinus molle*, a colourless oil, D^{15} 0·8583, $\alpha_D + 44·83°$, ester number 7·2; that from the fruit was pale yellow, D^{15} 0·8600, $\alpha_D + 42·5°$, ester number 25·2, after acetylation 56·5; both these oils give strong phellandrene reactions.

Oil from the leaves and flowers of *Buddleia perfoliata* from Mexico: a pleasant, although peculiar, smelling pale yellow oil, D^{15} 0·8862, a_D $-25°$, acid number 0·6, ester number 8·1.

Oil from Vitex agnus castus.—The leaves of this plant give 0·48% of a brown oil, which has an odour resembling hyssop, D^{15} 0·9010, a_D 7·92°, acid number 6·4, ester number 18·3, after acetylation 58·4; it contained cineol and probably sabinene. J. V. E.

Transformations of Chlorophyll under the Influence of Acids. LAD. HILDT, LEON MARCHLEWSKI, and J. ROBEL (*Bull. Acad. Sci. Cracow*, 1908, 261—296. Compare Willstätter and Hocheder. Abstr., 1907, i, 784).—The conclusion is drawn that chlorophyllan, phæophytin, and phyllogen are identical. The two last are obtained by the action of acids on chlorophyll at low temperatures and as a rule contain no phyllocyanin or other decomposition product which is not extracted from the ethereal solution by 15% hydrochloric acid. Phæophytins containing strongly basic products have been obtained, for example, from Acacia leaves. Chlorophyllan is usually obtained at higher temperatures, and can therefore contain decomposition products, but phyllogens have been prepared which react with 15% hydrochloric acid in exactly the same manner as chlorophyllans, and thus the chief difference between the two groups is removed. J. J. S.

Conversion of Phyllotaonin into Phytorhodins. T. KOŹNIEWSKI and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1908, 247—261; *Biochem. Zeitsch.*, 1908, **10**, 472—485).—It is shown by means of spectroscopic measurements that *allo*phyllotaonin is converted, under the influence of acids at high temperatures, into substances which are identical with Willstätter and Mieg's phytorhodins (Abstr., 1907, i, 69). The conversion of alkachlorophyll into these compounds thus takes place in two stages, the intermediate product being *allo*phyllotaonin. Phyllotaonin and *allo*phyllotaonin are much more closely related to alkachlorophyll than are the phytorhodins.

A very marked difference exists in the behaviour of phyllotaonin and the phytorhodins towards alkalis at high temperatures. Phyllotaonin is the best source for the preparation of phylloporphyrin, whereas phytorhodins do not yield this compound when heated with alkali at 200° under pressure. J. J. S.

Phæophytin and Chlorophyllan with some Concluding Remarks on Phylloxanthin. M. TSVETT (*Biochem. Zeitsch.*, 1908, **10**, 404—413).—The dark green precipitate which is formed from chlorophyll solutions by the addition of organic acids or of traces of hydrochloric acid (Tschirsch's chlorophyllan, Willstätter's phæophytin) is a mixture of the immediate products formed by the action of acid on chlorophyll, that is, a mixture, according to the author, of the already described α- and β-chlorophyllans; at any rate, it can by the absorption-analysis method be separated into constituents with the same spectroscopic properties and chemical reactions. By throwing it into Frémy's diphasic ethyl ether hydrochloric acid mixture, it gives the so-called phylloxanthin, which is apparently unchanged β-chlorophyllan and remains in ethereal solution, and the so-called phyllocyanin, which is not unchanged α-chlorophyllan, but a mixture that can be resolved into its components by Willstätter's method of acid fractionation. S. B. S.

The Nature of the So-called Crystallisable Chlorophyll ("Metachlorophyllin"). M. Tsvett (*Biochem. Zeitsch.*, 1908, **10**, 414—425).—The so-called "crystallisable chlorophyll" (α-metachlorophyllin) is not a natural constituent of chlorophyll, but an artifact, which is formed by the slow extraction of plants, and is formed from the genuine chlorophyllin under the influence of some unknown factor in the cell mechanism. Chlorophyll extracts immediately after preparation are free from this substance. In its spectrum, it combines the bands of both chlorophyllins (α and β), and must be considered as derived from both. S. B. S.

A New System of the So-called Chlorophyll Derivatives. M. Tsvett (*Biochem. Zeitsch.*, 1908, **10**, 426—429).—According to this system there are two main constituents of chlorophyll extract, namely, α-chlorophyllin and β-chlorophyllin. By the action of alkalis at low temperatures they yield respectively α- and β-chlorophyllic acids. The former of these, on treatment with alkali at 200°, yields Willstätter's rhodophyllin (from which by the action of acids alloporphyrin is obtained), whereas the latter under the same conditions yields phylloporphyrin. On treatment with weak acids, α-chlorophyllin yields chlorophyllan, from which, by the action of strong acids, Schunck's phyllocyanin is obtained. This on further treatment by acid, yields Willstätter's phytochlorins and phytorhodins. β-Chlorophyllin, on treatment with weak acids, yields β-chlorophyllan (Tschirch and Schunck's phylloxanthin), from which by more energetic hydrolysis the phytochlorins and phytorhodins are obtainable. These latter substances are obtainable directly from chlorophyllic acid by energetic hydrolysis. S. B. S.

Theory of Mordant Dyes. Leo A. Tschugaeff (*Ber.*, 1908, **41**, 2245—2246).—Polemical. A reply to Liebermann (this vol., i, 441). W. R.

Theory of Mordant Dyes. Alfred Werner (*Ber.*, 1908, **41**, 2383—2386).—A reply to Liebermann (this vol., i, 441). G. Y.

Blue Erythrosin Silver. Lüppo-Cramer (*Zeitsch. Chem., Ind. Kolloide*, 1908, ii, 325—326).—When silver nitrate is added to an excess of a dilute solution of erythrosin, a much more intensely coloured colloidal solution of the silver salt of erythrosin is obtained. The colour of the colloidal solution is distinctly more blue than the original. On boiling or on keeping for some time, the solution becomes opalescent, and the erythrosin silver compound, which has a pure blue colour, gradually separates.

The same thing can be observed in the presence of silver bromide or chloride, which act as protective colloids. The separated erythrosin silver compound when shaken up with water forms a very fine suspension. which can be filtered through paper without leaving a residue.

Fluorescein, dibromofluorescein, eosin, and tetraiododichlorofluorescein behave differently from erythrosin; the colloidal solutions of the silver salts in presence of colloidal silver bromide appear to be quite stable. H. M. D.

Rosocyanin. LATHAM CLARKE and C. LORING JACKSON (*Amer. Chem. J.*, 1908, **39**, 696—719).—Rosocyanin, the red colouring matter produced in the well-known test for boric acid with turmeric paper, has been studied by Schlumberger (*Bull. Soc. chim.*, 1866, [ii], **5**, 194) and by Ivanow-Gajewski (this Journ., 1873, 504, 760).

In the present investigation, the rosocyanin was prepared by heating an alcoholic solution of curcumin with boric and sulphuric acids, and was obtained as a purple powder with a yellowish-green metallic lustre. It does not melt, but decomposes at 200—230°. The statement of Schlumberger and Ivanow-Gajewski that the substance does not contain boron is confirmed. Rosocyanin has the composition $C_{14}H_{14}O_4$, and is thus isomeric with curcumin. It yields only mono-salts with the alkalis, whereas curcumin gives both mono- and di-salts. It is evident, therefore, that the former substance only contains one hydroxyl group. The *ammonium*, *potassium*, and *barium* salts are blue. The *acetyl* derivative forms a brownish-red powder. The *methyl ether* is obtained as a purple powder resembling rosocyanin itself.

When a mixture of curcumin, boric acid, and alcohol is left for eight hours, a red solution is obtained, from which ether precipitates a red powder, which is decomposed by water into rubrocurcumin and boric acid. If a mixture of curcumin, boric acid, and alcohol in certain proportions is left for some hours and then poured into water, *rubrocurcumin*, $C_{14}H_{14}O_4$, is obtained as a vermilion-coloured powder; it is unstable, gradually changing into curcumin, and, when heated at 200—240°, is converted into rosocyanin. *Acetylrubrocurcumin*,

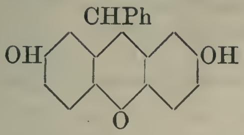
$$C_{14}H_{13}O_3{\cdot}OAc,$$

m. p. 245°, forms orange-yellow, prismatic needles.

Curcumin methyl ether, $C_6H_3(OMe)_2{\cdot}C_7H_7O_2$, m. p. 145°, forms small, orange-yellow needles, and, on oxidation with potassium permanganate, yields veratric acid.

Protocurcumin, $C_6H_3(OH)_2{\cdot}C_7H_7O_2$, formed by the removal of a methyl group from curcumin, gives a crimson coloration when treated with boric acid, sulphuric acid, and alcohol, which is turned blue by alkali hydroxides. This substance will be described in a future paper. E. G.

Condensation Products of Quinol. RICHARD MEYER and KARL WITTE (*Ber.*, 1908, **41**, 2453—2459).—A condensation product differing from that described by Schorygin (Abstr., 1907, i, 1031) is obtained by adding small quantities of benzaldehyde to a solution of quinol in dilute sulphuric acid. From its chemical behaviour and from the results of analysis and mol.-wt. determinations, the compound so formed is evidently 2 : 7-*dihydroxyphenylxanthen*, annexed formula. It crystallises in glittering, slender, colourless needles, m. p. 259° (decomp.); the *acetate*, $C_{19}H_{12}O(OAc)_2$, crystallises in glistening, slender, white needles, m. p. 200° (decomp.); the *benzoate*, $C_{19}H_{12}O(OBz)_2$, forms slender needles, m. p. 237°; the *dimethyl ether*, $C_{19}H_{12}O(OMe)_2$, forms small, colourless crystals, m. p. 132°; the *diethyl ether*, $C_{19}H_{12}O(OEt)_2$, crystallises in slender, white needles, m. p. 100—101°; the *dibenzyl ether*, $C_{19}H_{12}O(O\cdot CH_2Ph)_2$, forms stellate groups of small needles, m. p. 190°.



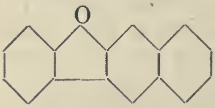
The acetate is oxidised by chromic acid, yielding the *carbinol*, $O{<}{\substack{C_6H_3(OAc)\\C_6H_3(OAc)}}{>}CPh\cdot OH$, m. p. 171—172°; the corresponding *benzoate*, $C_{19}H_{12}O_2(OBz)_2$, has m. p. 209°.

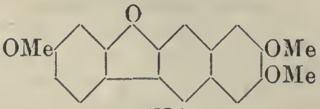
Condensation products of quinol with formaldehyde, acetaldehyde, chloral, &c., could not be isolated in a pure state.

Succinic anhydride (1 mol.) when heated with quinol (2 mols.) yields a *succinein*, $CO{<}{\substack{C_2H_4\\O}}{>}C{<}{\substack{C_6H_3(OH)_2\\C_6H_3(OH)_2}}$; it crystallises in slender, white needles, m. p. 217°. The *acetate*, $C_{16}H_{10}O_3(OAc)_2$, forms small, white crystals, m. p. 161—162°. The corresponding benzoate could not be obtained; in all cases, quinol dibenzoate was formed. Attempts to prepare the dihydroxy-compound corresponding with the acetate were also unsuccessful. W. H. G.

Pyronone Syntheses by means of the "Tertiary Bases Reaction." I. EDGAR WEDEKIND and JOHANNES HAEUSSERMANN (*Ber.*, 1908, **41**, 2297—2302).—The term "tertiary bases reaction" is used to denote the condensation of acyl halides by means of tertiary bases, a reaction which led to the production of dehydracetic acid from acetyl chloride (Wedekind, Abstr., 1902, i, 739, compare also Wedekind and Weisswange, Abstr., 1906, i, 437). The authors have now studied the action of tripropylamine on propionyl chloride, and have obtained a product the molecular weight of which is three times that of monomethylketen (which may be formed as an intermediate compound, compare Staudinger and Klever, this vol., i, 318), but it is not identical with trimethylphloroglucinol. The substance is probably formed by loss of 2HCl from 3 mols. of propionyl chloride, forming the compound $COEt\cdot CHMe\cdot CO\cdot CHMe\cdot COCl$, which is partly transformed into the enolic modification, and loses hydrogen chloride, thus: $CO{<}{\substack{CHMe\cdot COCl\\CMe{:}CEt\cdot OH}} \longrightarrow CO{<}{\substack{CHMe\cdot CO\\CMe{:}CEt}}{>}O$, giving 3 : 5-*dimethyl-2-ethyl-*4 : 6-*pyronone*. This separates from glacial acetic acid in monoclinic crystals, m. p. 151°. On heating with alkalis under pressure, it is decomposed into propionic acid and diethyl ketone, and an acetic acid solution absorbs bromine. J. C. C.

Brazan from Naphthalene. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1908, **41**, 2373—2377).—The constitution (I) for brazan suggested by Kostanecki and Lloyd (Abstr., 1903, i, 645) is supported by the following facts: (1) Those transformation products which in the brazilin series yield brazan, in the hæmatoxylin series form naphthalene. (2) 2 : 7 : 8-Trimethoxybrazan (II) behaves towards concentrated sulphuric acid in the same manner as its analogue, 5-methoxy-2-methylcoumarone (III).


(I.)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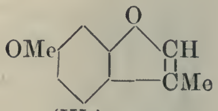
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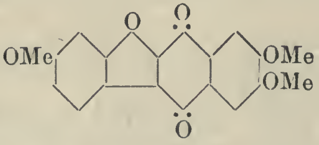
(3) 2 : 7 : 8-Trimethoxybrazanquinone (IV), obtained from 5- or 10-hydroxy-2 : 7 : 8-trimethoxybrazan (V), behaves as a *p*-quinone.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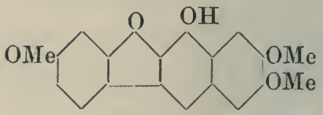
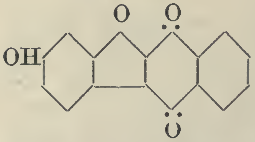

(V.)

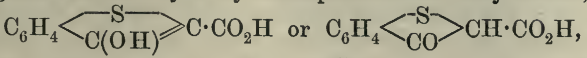
Hence, brazan contains a naphthalene and a coumarone nucleus, and is a $\beta\beta$-derivative of naphthalene. The constitution of brazan has now been confirmed by syntheses.

Liebermann (Abstr., 1899, i, 523) prepared anhydro-α-naphthaquinoneresorcinol (2-hydroxybrazanquinone, annexed formula) from 2 : 3-dichloro-α-naphthaquinone. The 2-hydroxy-compound crystallises in orange-yellow needles, m. p. 320°, gives a bluish-green coloration with concentrated sulphuric acid, and is converted by methyl sulphate and alkalis into 2-*methoxybrazanquinone*, $C_{17}H_{10}O_4$, crystallising in golden leaflets, m. p. 290°. This resembles 2 : 7 : 8-trimethoxybrazan in that it distils unchanged when carefully heated and behaves like the hydroxy-compound towards concentrated sulphuric acid. When heated with hydriodic acid, 2-methoxybrazanquinone yields 2-*hydroxybrazan*, $C_{16}H_{10}O_2$, which forms white crystals, m. p. 255°, gives a green coloration with alcoholic ferric chloride, and dissolves in sodium hydroxide to a colourless solution with blue fluorescence. 2-*Acetoxybrazan*, $C_{18}H_{12}O_3$, white needles, m. p. 196—197°, has a slight blue fluorescence in alcoholic solution. 2-Methoxybrazan, $C_{17}H_{12}O_2$, prepared by the action of methyl sulphate and alkalis on the hydroxy-compound, crystallises in white leaflets, m. p. 205—206°, and gives colorations with ferric chloride and sulphuric acid. Brazan, m. p. 202°, is obtained when 2-hydroxybrazan or 2-hydroxybrazanquinone is distilled with zinc dust.

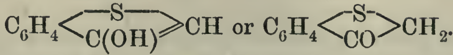


G. Y.

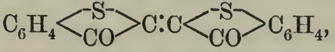
Preparation of a Red Colouring Matter of the Thionaphthen Series. Kalle & Co. (D.R.-P. 194237 and 194254).—Phenylthioglycol-*o*-carboxylic acid, when treated with condensing agents or when heated, gives rise to 3-hydroxythionaphthen-2-carboxylic acid,



$$C_6H_4<\substack{S\\C(OH)}>C\cdot CO_2H \text{ or } C_6H_4<\substack{S\\CO}>CH\cdot CO_2H,$$

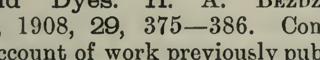
and 3-hydroxythionaphthen,  $C_6H_4<\substack{S\\C(OH)}>CH$ or $C_6H_4<\substack{S\\CO}>CH_2$.

When either of these compounds is oxidised with ferric chloride or potassium dichromate in the presence of alkali and the solution then acidified, a red colouring matter is precipitated. This product probably has the following constitution:

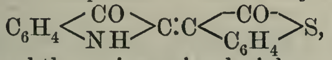


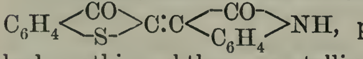
$$C_6H_4<\substack{S\\CO}>C:C<\substack{S\\CO}>C_6H_4,$$

and resembles indigotin in its chemical properties; it furnishes a colourless leuco-derivative, which is again converted into the colouring matter by aerial oxidation. The red colouring matter is also produced on warming 3-hydroxythionaphthen with sulphur or by adding milk of sulphur to an alkaline solution of 3-hydroxythionaphthen-2-carboxylic acid. In the latter case, the dye is precipitated with acid. G. T. M.

Indigoid Dyes. I. PAUL FRIEDLÄNDER (*Monatsh.*, 1908, 29, 359—374. Compare Abstr., 1906, i, 378; 1907, i, 334; this vol., i, 200, 371).—The author has prepared further members of this class of dyes (compare also following abstracts), of which a general account is given. In addition to the work previously published (compare also Bezdzik, Friedländer, and Koeniger, this vol., i, 200), the following is new. "Leucothioindigotin" (Abstr., 1907, i, 335) forms a *diacetyl* derivative, $C_{16}H_8O_2S(COMe)_2$, colourless, glistening needles, m. p. 240°. "2:3-*Bisthionaphthenindigotin*" (thioindirubin) [2:3′-*bisoxythionaphthen*],  $C_6H_4<\substack{CO\\S}>C:C<\substack{CO\\C_6H_4}>S$, formed by condensing hydroxythionaphthen with thionaphthenquinone in glacial acetic acid solution with addition of a little hydrochloric acid, crystallises in red needles, m. p. 205—207°. J. C. C.

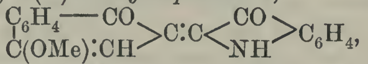
Indigoid Dyes. II. A. BEZDZIK and PAUL FRIEDLÄNDER (*Monatsh.*, 1908, 29, 375—386. Compare preceding abstract).—A detailed account of work previously published (Friedländer, this vol., i, 371, 372). The following is new:

"3-*Thionaphthen-2-indole-indigotin*" [2′-*indoxyl-3-thionaphthen-2′-one*],  $C_6H_4<\substack{CO\\NH}>C:C<\substack{CO\\C_6H_4}>S$, prepared by heating indoxyl with thionaphthenquinone in glacial acetic acid solution, crystallises from xylene in violet-black needles, m. p. 247—250°, which sublime at a higher temperature.

"2-*Thionaphthen-3-indole-indigotin*" [3′-*indoxyl-2-thionaphthen-3-one*],  $C_6H_4<\substack{CO\\S}>C:C<\substack{CO\\C_6H_4}>NH$, prepared similarly from isatin and hydroxythionaphthen, crystallises from nitrobenzene in small, red needles, which do not melt at 270°, and sublime at a higher temperature. The dye (thioindigo-scarlet) forms a pale yellow *leuco*-compound, from which textile fibres are dyed scarlet. An improved method of preparing 2′-indoxyl-3-thionaphthen-2′-one consists in condensing isatin chloride and hydroxythionaphthen in benzene solution in presence of phosphoryl chloride. It is also formed by heating together α-isatinanilide and hydroxythionaphthen either in petroleum or in acetic anhydride. 1-Oxy-2:(2′)-indoxylnaphthalene is best prepared by condensing α-isatinanilide with α-naphthol in acetic anhydride solution. When prepared from isatin chloride (this vol., i, 372), an isomeric *dye*, $\mathrm{CO}<\genfrac{}{}{0pt}{}{-\mathrm{C_6H_4}-}{\mathrm{CH{:}CH}}>\mathrm{C{:}C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{NH}}>\mathrm{C_6H_4}$, is also formed, which crystallises from glacial acetic acid in compact prisms, resembling potassium permanganate. It forms a brownish-yellow *acetyl* derivative, crystallising from glacial acetic acid in compact, glistening needles. When isatin chloride is condensed with 2-chloro-α-naphthol, a *dye*, $\mathrm{CO}<\genfrac{}{}{0pt}{}{-\mathrm{C_6H_4}-}{\mathrm{CH{:}CCl}}>\mathrm{C{:}C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{NH}}>\mathrm{C_6H_4}$, is obtained, which crystallises from glacial acetic acid in brassy, dark prisms.

1-*Oxy*-2:(3′)-*indoxylnaphthalene*, $\mathrm{CH}<\genfrac{}{}{0pt}{}{\mathrm{CH{\cdot}CO}}{-\mathrm{C_6H_4}-}>\mathrm{C{:}C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{NH}}>\mathrm{C_6H_4}$, prepared by condensing isatin chloride with β-naphthol in benzene solution, crystallises from xylene in blackish-violet, glistening needles.

4-*Methoxy*-1-*oxy*-2-(2′)*indoxylnaphthalene*,



$$\genfrac{}{}{0pt}{}{\mathrm{C_6H_4}\text{——}\mathrm{CO}}{\mathrm{C(OMe){:}CH}}>\mathrm{C{:}C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{NH}}>\mathrm{C_6H_4},$$

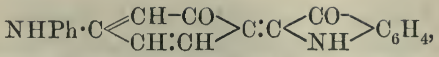
prepared by condensing 4-methoxy-α-naphthol with α-isatinanilide in acetic anhydride solution, forms bluish-black, glistening needles.

8-*Oxy*-7-*indoxylacenaphthene*, $\genfrac{}{}{0pt}{}{\mathrm{CO}\text{—}}{\mathrm{C_{10}H_6}}>\mathrm{C{:}C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{NH}}>\mathrm{C_6H_4}$, is obtained by condensing indoxyl with acenaphthenequinone in glacial acetic acid solution. It forms coppery needles; from the *leuco*-compound, reddish-violet shades on textile fibres are obtained. The *sulphonic acid* of the dyestuff gives a reddish-violet solution in water.

8-*Oxy*-7-*oxythionaphthenylacenaphthene*, $\genfrac{}{}{0pt}{}{\mathrm{CO}\text{—}}{\mathrm{C_{10}H_6}}>\mathrm{C{:}C}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{S}}>\mathrm{C_6H_4}$, prepared by condensing hydroxythionaphthen with acenaphthenequinone in glacial acetic acid solution, crystallises from nitrobenzene in brick-red, glistening needles. By the use of the *leuco*-compound, textile fibres are dyed red. J. C. C.

Indigoid Dyes. III. Paul Friedländer and R. Schuloff (*Monatsh.*, 1908, **29**, 387—393. Compare preceding abstracts).—4-*Hydroxy*-1-*indoxylbenzene*, $\mathrm{HO{\cdot}C}<\genfrac{}{}{0pt}{}{\mathrm{CH{-}CO}}{\mathrm{CH{:}CH}}>\mathrm{C{:}C}<\genfrac{}{}{0pt}{}{\mathrm{CO}-}{\mathrm{NH}}>\mathrm{C_6H_4}$, prepared by condensing isatin chloride with resorcinol in benzene solution, crystallises from alcohol in bronzy, dark violet needles. It forms a *sulphonic acid*. 4-*Methoxy*-1-*indoxylbenzene*, similarly obtained from resorcinol monomethyl ether, forms brownish-violet needles, m. p. 162°. The *sulphonic acid* is red. On warming with dilute sodium hydroxide the dye yields *o*-hydroxyanisaldehyde.

4-*Anilino*-1-*indoxylbenzene*,



$\mathrm{NHPh{\cdot}C}<\!\begin{array}{l}\mathrm{CH{-}CO}\\ \mathrm{CH{:}CH}\end{array}\!>\mathrm{C{:}C}<\!\begin{array}{l}\mathrm{CO{-}}\\ \mathrm{NH}\end{array}\!>\mathrm{C_6H_4}$,

prepared by condensing isatin chloride with *m*-hydroxydiphenylamine in benzene solution, forms violet needles.

3-*Hydroxy*-1-*indoxylbenzene*, similarly prepared from catechol, forms violet-black needles, m. p. 245° (decomp.). It dyes iron- and chrome-mordanted cotton in greenish-blue shades. 3 : 4-*Dihydroxy*-1-*indoxylbenzene*, obtained from pyrogallol, forms blackish-violet needles and gives bluish-violet shades on iron- and chrome-mordanted cotton. The *sulphonic acid* is red. J. C. C.

Constitution of Neosine. D. Ackermann and Friedrich Kutscher (*Zeitsch. physiol. Chem.*, 1908, **56**, 220—222).—Neosine, $C_6H_{17}O_2N$, from meat-extract, yields on distillation with baryta, trimethylamine, and is perhaps a homologue of choline. G. B.

Tropine. Ernst Schmidt and A. Kircher (*Chem. Zentr.*, 1908, i, 1467; from *Pharm. Post.*, 1907, **40**, 771—772).—The authors show that the tropine bromide prepared directly from tropine is identical with α-tropidine hydrobromide, ($C_8H_{14}BrN,HBr$); it forms colourless, needle-shaped crystals, m. p. 216—217°, and gives an *aurichloride*, $C_8H_{14}BrN,HAuCl_4$, which crystallises in yellow needles, m. p. 170°, and a *platinichloride*, $(C_8H_{14}BrN)_2,H_2PtCl_6$, which crystallises in long, red needles, blackening at 210°, and m. p. 215—216°. Silver nitrate decomposes the bromide, removing hydrogen bromide; the product gives a crystalline, anhydrous *platinichloride*, $(C_8H_{13}N)_2,H_2PtCl_6$, m. p. 160—161° (decomp.), and is not identical with that obtained from tropidine. J. V. E.

Synthesis of Amino-acids. VII. Proline (Pyrrolidine-2-carboxylic Acid). Sören P. L. Sörensen and A. C. Andersen (*Zeitsch. physiol. Chem.*, 1908, **56**, 236—249. Compare Abstr., 1903, i, 833; 1905, i, 600, 749; Willstätter, 1900, i, 405; Fischer, 1901, i, 745).—A good yield of pyrrolidine-2-carboxylic acid is obtained by boiling ethyl γ-bromopropylphthaliminomalonate with alcoholic sodium hydroxide and evaporating the product with hydrochloric acid. The acid is isolated and purified by means of its copper salt.

Proline is not formed when arginine is hydrolysed with barium hydroxide solution. Under suitable conditions, the amount of ornithine obtained during the hydrolysis is 64% of that required by Schultze and Winterstein's equation: $NH:C(NH_2)\cdot NH\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H + H_2O \longrightarrow NH_2\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H + CO(NH_2)_2$. J. J. S.

New Method of Preparing Bromoacetonitrile and its Addition to Tertiary Bases. Julius von Braun (*Ber.*, 1908, **41**, 2113—2123. Compare this vol., i, 625).—The interaction of cyanogen bromide and tertiary bases according to the equation $RR'NR'' + BrCN = RR'N\cdot CN + R''Br$, has hitherto been applied chiefly to the preparation of secondary bases (compare Abstr., 1904, i, 344, 687; this vol., i, 626, 684, and Sachs and Weigert, Abstr., 1907, i, 1046), but it also affords a means of preparing alkyl bromides that are not readily obtained directly, provided that the tertiary base is readily accessible and has been prepared by some other method than the alkylation of a primary or secondary amine by an alkyl halide.

The use of dimethyl-, diethyl-, or dipropyl-aminoacetonitrile is not suitable for the ready preparation of pure bromoacetonitrile, and from his former researches (Abstr., 1907, i, 960) the author was led to employ piperidylacetonitrile, which was found to give good results. Bromoacetonitrile, being thus readily obtainable, has been employed in a number of reactions; in the present paper, its action towards tertiary aromatic amines and alkaloids is described. Whilst with tertiary aliphatic amines and cyclic bases, bromoacetonitrile yields normal additive products, with bases such as dimethylaniline it yields, for example, phenyltrimethylammonium bromide. The additive products which are formed with alkaloids, for example, atropine, codeine, strychnine, &c., although containing two new poisonous factors (quaternary character and cyanogen group), in addition to that inherent in the alkaloid, are relatively harmless.

When piperidyloacetonitrile (200—300 grams) is mixed with 1 mol. of cyanogen bromide and, after twenty-four hours, heated on the water-bath, dicyanomethylpiperidinium bromide, $C_5NH_{10}(CH_2\cdot CN)_2Br$, is formed. This is extracted with ether, the ethereal solution evaporated, and the residue distilled. The fraction distilling at 50—90°/15 mm. contains the bromoacetonitrile, which can be purified by redistillation. The following homologues of piperidinoacetonitrile were prepared: *a-Piperidyl-*n*-butyronitrile*, $C_5NH_{10}\cdot CHEt\cdot CN$ (from piperidine and propaldehydecyanohydrin or propaldehyde potassium cyanide and sodium hydrogen sulphite), colourless liquid, b. p. 88—91°/7 mm. *a-Piperidyl-*n*-hexonitrile*, $C_5NH_{10}\cdot CH(C_4H_9)\cdot CN$ (from piperidine and valeraldehyde), colourless liquid with a weak odour of valeraldehyde, b. p. 123°/12 mm. *a-Piperidyl-*n*-octonitrile*, $C_5NH_{10}\cdot CH(C_6H_{13})\cdot CN$ (from piperidine and heptaldehyde) is a colourless, viscous oil with a weak odour of heptaldehyde, b. p. 158—159°/9 mm. When these homologues of piperidylacetonitrile are treated with cyanogen bromide in the cold, only the hydrobromides of the compounds are formed; with water they are decomposed into the parent aldehyde, hydrogen cyanide, and piperidine hydrobromide. *a-Piperidyl-*n*-octonitrile hydrobromide* has m. p. 155°.

Bromoacetonitrile forms with triethylamine a *compound*,

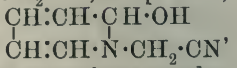
$$NEt_3Br\cdot CH_2\cdot CN,$$

m. p. 202° (decomp.), with tripropylamine a *compound*,

$$NPr^{\alpha}_3Br\cdot CH_2\cdot CN,$$

m. p. 167° (decomp.), with phenylpiperidine a *compound*,

$$C_5NH_{10}PhBr\cdot CH_2\cdot CN,$$

m. p. 171°, with pyridine a *compound*, $C_5NH_5Br\cdot CH_2\cdot CN$, m. p. 160°, giving with alkalis a yellow *precipitate*, probably 
$$\begin{array}{l}\text{CH:CH}\cdot\text{CH}\cdot\text{OH}\\ \vert\qquad\qquad\quad\vert\\ \text{CH:CH}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CN}\end{array},$$
which is converted on warming into a greyish-green, amorphous *powder*, softening at 120°, m. p. 150°, corresponding with the composition $C_{14}H_{14}ON_4$, but which may be a mixture. With *iso*quinoline, bromoacetonitrile gives a *compound*, $C_9NH_7Br\cdot CH_2\cdot CN$, m. p. 195°, yielding

a red *precipitate* with alkalis, which is at once partly converted into a reddish-yellow *powder*, softening at 150°, m. p. 160°.

Bromoacetonitrile gives with tropine a *compound*,

$$C_8H_{15}ONBr\cdot CH_2\cdot CN,$$

blackening at 215°, m. p. 225°, with atropine a very hygroscopic *compound*, the *platinichloride* of which, $(C_{17}H_{23}O_3N\cdot CH_2\cdot CN)_2PtCl_6$, forms small, red crystals, m. p. 215°, with cocaine a *compound*,

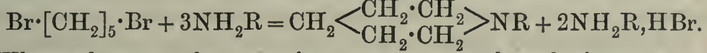
$$C_{17}H_{21}O_4NBr\cdot CH_2\cdot CN,$$

m. p. 169° (decomp.), with papaverine a *compound*,

$$C_{20}H_{21}O_4NBr\cdot CH_2\cdot CN,$$

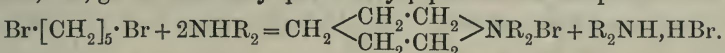
m. p. 204°, with codeine a *compound*, $C_{18}H_{21}O_3NBr\cdot CH_2\cdot CN$, m. p. 189°, and with strychnine a *compound*, $C_{21}H_{22}O_2N_2Br\cdot CH_2\cdot CN$, m. p. 275°. J. C. C.

Characterisation of Primary, Secondary, and Tertiary Bases by the Aid of αε-Dibromo-*n*-pentane. JULIUS VON BRAUN (*Ber.*, 1908, **41**, 2156—2165).—The author shows that αε-dibromo-*n*-pentane is an excellent agent for characterising the three classes of amines. Primary amines, in which the nitrogen is attached to an open chain, a hydrogenised carbon ring, a heterocyclic ring, or a benzene ring not substituted in the ortho-position, give with it tertiary piperidines:



$$Br\cdot[CH_2]_5\cdot Br + 3NH_2R = CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>NR + 2NH_2R,HBr.$$

When a benzene ring contains one or two ortho-substituents, pentamethylenediamine derivatives are formed (Scholtz and Wassermann, Abstr., 1907, i, 339). Secondary amines of the aliphatic or piperidine series, &c., give exclusively quaternary piperidinium compounds:



$$Br\cdot[CH_2]_5\cdot Br + 2NHR_2 = CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>NR_2Br + R_2NH,HBr.$$

In the case of secondary aromatic bases, small amounts of tertiary pentamethylenediamine bases are also formed, and when the benzene ring contains an ortho-substituent, the latter constitute the sole product.

Tertiary amines, either aliphatic or aromatic, yield diammonium bromides, $Br\cdot[CH_2]_5\cdot Br + 2NR_3 = NR_3Br\cdot[CH_2]_5\cdot NR_3Br$, but they are readily characterised only when they consist of tertiary cyclic bases, such as pyridine, methylpiperidine, &c., for the derivatives of the tertiary aliphatic amines are usually very hygroscopic, and those of the aromatic bases are formed only very slowly.

The formation of tertiary piperidines by the aid of dibromopentane has already been the subject of several investigations (compare Abstr., 1904, i, 841; 1907, i, 960; Luft, Abstr., 1906, i, 118; Scholtz and Wassermann, *loc. cit.*), and the author now describes *camphylpiperidine*, $C_{10}H_{17}\cdot NC_5H_{10}$, b. p. 134—135°/10 mm., obtained by warming 3 mols. of camphylamine and 1 mol. of dibromopentane, the excess of the base being removed by means of benzenesulphonyl chloride, whereby *camphylamine benzenesulphonate*, a red, viscid oil, is formed. *Camphylpiperidine picrate*, $C_{15}H_{27}N,C_6H_3O_7N_3$, has m. p. 117°.

Diethylpiperidinium bromide, $C_5NH_{10}Et_2Br$, forms white, glistening leaflets, m. p. 257°, decomposing at this temperature into ethyl bromide and ethylpiperidine. The *platinichloride* forms small, reddish-yellow crystals, m. p. 240°.

Diisoamylpiperidinium bromide forms silvery, hygroscopic leaflets, m. p. 115°; the *aurichloride* has m. p. 177°, and the *platinichloride* blackens at 212° and has m. p. 216°.

With dibromopentane, methylaniline forms mostly *phenylmethylpiperidinium bromide*, $C_5NH_{10}PhMeBr$, m. p. 170°, with a small quantity of s-*diphenyldimethylpentamethylenediamine*,

$$NPhMe\cdot[CH_2]_5\cdot NPhMe,$$

m. p. 38°, b. p. 244—245°/8 mm., the *picrate* of which is described, and some phenylpiperidine. Ethylaniline gives, under the same conditions, *phenylethylpiperidinium bromide*, $C_5NH_{10}PhEtBr$, m. p. 217°, and s-*diphenyldiethylpentamethylenediamine*, $NPhEt\cdot[CH_2]_5\cdot NPhEt$, a pale yellow, viscous liquid, b. p. 257—259°/7 mm. Methyl-*o*-toluidine and dibromopentane yield only s-*di*-o-*tolyldimethylpentamethylenediamine*, $C_6H_4Me\cdot NMe\cdot[CH_2]_5\cdot NMe\cdot C_6H_4Me$, a viscous liquid, b. p. 229°/9 mm.; the *platinichloride* is a viscid, red oil, and the *picrate* has m. p. 184°.

From tetrahydroquinoline is obtained s-*bistetrahydroquinolylpentamethylenediamine*, $C_9NH_{10}\cdot[CH_2]_5\cdot C_9NH_{10}$, glistening crystals, m. p. 76°. The *picrate* softens at about 70°, and has m. p. below 90°.

Triethylamine and dibromopentane condense to a very hygroscopic *compound*, of which the *platinichloride* has m. p. 235°. Similar compounds are obtained from tripropyl-, tributyl-, and triamyl-amine.

1-Phenylpiperidine gives a pale red, hygroscopic *compound*; the *platinichloride*, $\{(C_5NH_{10}Ph)_2[CH_2]_5\}PtCl_6$, is a red, crystalline powder, m. p. 216°. Quinoline yields a yellowish-red, crystalline *powder*, $C_9NH_7Br\cdot[CH_2]_5\cdot C_9NH_7Br$, m. p. 200°, with previous sintering. Tropine gives a white *compound*, $C_{21}H_{40}O_2N_2Br_2$, m. p. 282°, and strychnine a white *compound*, $C_{47}H_{54}O_6N_4Br_2$, which does not melt at 300°. J. C. C.

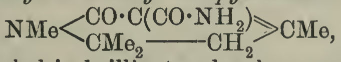
Stereoisomerism of Compounds Containing Asymmetric Carbon and Asymmetric Quinquevalent Nitrogen Atoms. Max Scholtz (*Ber.*, 1908, 41, 2005—2009).—The addition of an alkyl haloid to an active *N*-alkylated coniine, conhydrine (Abstr., 1904, i, 1044; 1905, i, 296), or 2-phenyl-6-methylpiperidine (Scholtz and Wassermann, Abstr., 1907, i, 340) results in the formation of two stereoisomeric quaternary ammonium compounds; active alkaloids, excepting the preceding, yield only one. Such isomerides have been obtained only from piperidine derivatives having a large substituent in position 2, and the theory is obvious that the existence of two stereoisomeric quaternary compounds is due to the influence of this substituent, which confers stability on the groups attached to the neighbouring nitrogen atom. To test the validity of the theory, α- and β-pipecoline have been converted into the *N*-ethyl derivatives, and, after resolution by tartaric acid, the *l*-forms of the tertiary base have been treated with benzyl bromide or iodide. In neither case have two isomerides been obtained. Moreover, the author showed some years ago (Abstr., 1901, i, 749) that active amyl iodide and 1-methyl-2-pipecoline yield only one additive product. Hence it appears that a methyl group, whether directly attached to the asymmetric nitrogen atom or in the α-position in the piperidine ring, cannot exert sufficient stabilising influence to ensure the formation of two stable stereoisomeric quaternary compounds.

Hohenemser and Wolffenstein resolved 1-ethyl-2-pipecoline by means of the hydrogen tartrate, and found that the salt of the *d*-base separated first (Abstr., 1899, i, 936); the author, using the same method, obtained the salt of the *l*-base first. The discrepancy is attributed to the influence of temperature. l-1-*Benzyl*-1-*ethyl*-2-*pipecolinium iodide*, m. p. 230°, has $[\alpha]_D$ $-52·5°$ in 10% alcoholic solution; the corresponding *bromide*, m. p. 237°, has $[\alpha]_D+20°$ in the same solvent. The bromide of the inactive base has m. p. 204°.

1-*Ethyl*-3-*pipecoline*, b. p. 145·5—146·5°, was resolved by tartaric acid, and the active base so obtained had D^{17} 0·8095 and $[\alpha]_D$ $-3·2°$. l-1-*Benzyl*-1-*ethyl*-3-*pipecolinium iodide*, m. p. 174°, crystallises in colourless needles. C. S.

Hydrolysis of Oxyhydropyridine Nitriles. Galeazzo Piccinini (*Atti R. Accad. Sci. Torino*, 1908, **43**, 547—558. Compare this vol., i, 51).—The nitriles described in the former paper are not attacked by hydrochloric acid below 120°. The hydrolysis can be arrested before the elimination of the carboxyl group by employing 95—96% sulphuric acid at 150° as the hydrolysing agent. The amide is thus obtained, and may be converted into the acid by alkalis.

1 : 4 : 6 : 6-*Tetramethyl*-Δ^3-*tetrahydro*-2-*pyridone*-3-*carboxylamide*,



$$NMe\!<\!\begin{array}{l}CO\cdot C(CO\cdot NH_2)\\CMe_2\text{——}CH_2\end{array}\!>\!CMe,$$

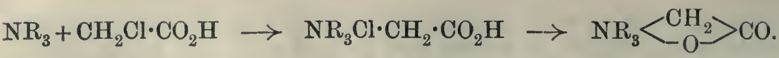
crystallises from alcohol in brilliant, colourless rosettes, or from water in large, monoclinic prisms, m. p. 195—196°. Its solution in water is neutral, but it dissolves readily in acids, and is precipitated by the usual reagents for alkaloids. Boiling with 50% sodium hydroxide solution is necessary to remove the NH_2 group. The corresponding *carboxylic acid*, $C_{10}H_{15}O_3N$, may be obtained by heating the nitrile with hydrochloric acid, D 1·19, for several hours at 120—125°, or by boiling the amide with 20% sulphuric acid, some decomposition of the acid occurring in the latter case, or best by the action of nitrous acid on the amide. It forms colourless prisms, m. p. 125—126° if rapidly, 118—120° (decomp.) if slowly, heated. The salts are readily soluble.

4 : 6 : 6-*Trimethyl*-Δ^3-*tetrahydro*-2-*pyridone*-3-*carboxylamide*,

$$C_9H_{14}O_2N_2,$$

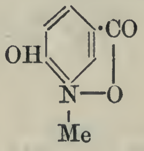
forms large, colourless prisms, m. p. 199—200° (corr.). Nitrous acid converts it into the *carboxylic acid*, $C_9H_{13}O_3N$, crystallising from water in long, colourless prisms, m. p. 116—117° (corr.). The *sodium* salt, $C_9H_{12}O_3NNa,2H_2O$, and the *barium* salt, $(C_9H_{12}O_3N)_2Ba,3H_2O$, are described. C. H. D.

New Betaines of the Pyridine Series. Alfred Kirpal (*Monatsh.*, 1908, **29**, 471—484).—According to Liebreich (*Ber.*, 1869, **2**, 12), betaines are formed when tertiary bases are heated with chloroacetic acid and the products shaken with silver oxide:

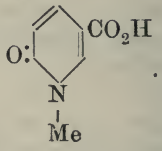


$$NR_3 + CH_2Cl{\cdot}CO_2H \longrightarrow NR_3Cl{\cdot}CH_2{\cdot}CO_2H \longrightarrow NR_3{<}\begin{smallmatrix}CH_2\\O\end{smallmatrix}{>}CO.$$

It is found now that, when heated with chloroacetic acid and treated with sulphuric acid, hydroxypyridinecarboxylic acids yield products which, according to the above scheme, should be the corresponding betaines, $CO_2H{\cdot}C_5NH_3(OH){<}\begin{smallmatrix}CH_2\\O\end{smallmatrix}{>}CO$. This structure, however, appeared doubtful, as on titration the products behaved as dibasic acids. Meyer has shown (Abstr., 1906, i, 108) that the action of methyl iodide on 6-hydroxynicotinic acid in alkaline solution leads to the formation, not of the expected betaine (I), but of the *N*-methyl derivative of the keto-acid (II).

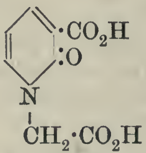


(I.)

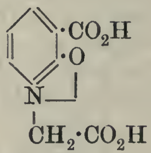


(II.)

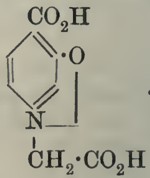
In analogy to this, the product obtained from 2-hydroxynicotinic acid and chloroacetic acid might have the formula (III) or (IV), there being, similarly, two possibilities for the constitution of the product from 4-hydroxynicotinic acid, but that from 3-hydroxy*iso*nicotinic acid, if not a betaine, can have only the formula (V).



(III.)

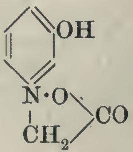


(IV.)

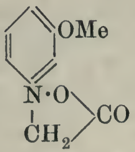


(V.)

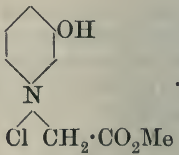
It has been found, however, that 3-hydroxypyridinebetaine (VI) acts towards alkalis as a monobasic acid, and forms a silver salt, which with methyl iodide yields a methyl derivative; this does not react with ammonia, and must therefore be the ether (VII) (this vol., ii, 436). In agreement with this, it is found that the additive compound of 3-hydroxypyridine and methyl chloroacetate (VIII), on treatment with silver oxide, yields the betaine (VI), and not a chlorine-free methyl ester.



(VI.)



(VII.)



(VIII.)

The products obtained from the hydroxypyridinecarboxylic acids are therefore considered to be betaines, the second mol. of alkali being neutralised by the hydroxyl.

In connexion with the formation of methyl iodide when pyridine betaine is treated according to the Herzig-Meyer method (this vol., ii, 436), it is observed that von Gerichten found that pyridinebetaine hydrochloride, when heated at 200°, decomposes, forming pyridine, carbon dioxide, and methyl chloride (Abstr., 1882, 1109).

The *additive* compound of 3-hydroxypyridine and chloroacetic acid, $OH\cdot C_5NH_4Cl\cdot CH_2\cdot CO_2\cdot C_5NH_4(OH)\cdot CH_2\cdot CO_2H$, crystallises in colourless needles, m. p. 185° (decomp.). 3-Hydroxypyridinebetaine, $C_7H_7O_3N,H_2O$, crystallises in colourless, rhombic plates, m. p. 182° (decomp.). The silver salt, $2C_7H_6O_3NAg,3H_2O$, was analysed. The methyl ester, $C_8H_9O_3N$, forms needles, m. p. 160° (decomp.).

The *additive* compound of 3-hydroxypyridine and methyl chloroacetate, $C_8H_{10}O_3NCl$, forms colourless plates, m. p. 155° (decomp.); the *platinichloride*, $(C_8H_9O_3N)_2,H_2PtCl_6,2H_2O$, crystallises in orange-yellow plates, m. p. 205°.

2-Hydroxynicotinic acid betaine (*2-hydroxy-3-carboxypyridinebetaine*), $C_8H_7O_5N$, crystallises in needles, m. p. 240°.

3-Hydroxy-4-carboxypyridinebetaine, prepared from 3-hydroxy*iso*nicotinic acid, crystallises in needles, m. p. 200° (decomp.).

4-Hydroxy-3-carboxypyridinebetaine, prepared from 4-hydroxynicotinic acid, forms plates, m. p. 220° (decomp.). G. Y.

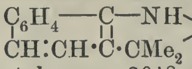
Quinoline-2-carboxyl Chloride. EMIL BESTHORN (*Ber.*, 1908, 41, 2003—2004).—The difference between Meyer (Abstr., 1905, i, 155, 666) and Besthorn and Ibele (Abstr., 1905, i, 612; 1906, i, 605) as to the physical properties of quinoline-2-carboxyl chloride is due to the fact that Kahlbaum's thionyl chloride contains a not inconsiderable amount of stannic chloride, which reacts with quinoline-2-carboxylic acid to form a substance insoluble in organic solvents. When thionyl chloride, free from tin, reacts with quinoline-2-carboxylic acid, the chloride, m. p. 97—98°, is obtained, the molecular weight of which, determined in benzene by the cryoscopic method, agrees with the formula $C_{10}H_6ONCl$. Meyer's chloride probably contained tin.

The presence of tin chloride in thionyl chloride is detected by the yellow colour produced by triphenylmethyl chloride, or by the splendid red coloration produced by *p*-tri-iodotriphenylmethyl chloride. A coloration is not produced in either case if pure thionyl chloride is used. C. S.

2-Quinolyl Phenyl Ketone. EMIL BESTHORN (*Ber.*, 1908, 41, 2001—2003).—The reaction between quinoline-2-carboxyl chloride and aluminium chloride in dry benzene leads to the formation of *2-quinolyl phenyl ketone*, $C_9NH_6\cdot COPh$, m. p. 110—111°, in good yield. The substance is colourless, and shows no tendency to yield dyes; consequently, it is doubtful whether the red substance, $C_{19}H_{12}ON_2$, obtained by Besthorn and Ibele (Abstr., 1904, i, 527) is 2 : 2′-diquinolyl ketone. C. S.

Indolinones. D. LIEBER (*Monatsh.*, 1908, 29, 421—429).—Brunner has shown that the phenylhydrazides of fatty acids, or phenyl-substituted fatty acids, are converted into indolinones when heated with calcium oxide (Abstr., 1907, i, 240). This reaction has now been applied to the formation of indolinones from the α- and β-naphthylhydrazides of *iso*butyric acid.

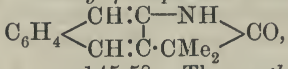
iso*Butyryl-α-naphthylhydrazide*, $C_{10}H_7\cdot NH\cdot NH\cdot C_4H_7O$, is obtained in a 86 3% yield by the action of *iso*butyric anhydride on α-naphthylhydrazine in benzene solution and extraction with water of the α-naphthylhydrazine *iso*butyrate, which is simultaneously formed. When heated with calcium oxide at 230°, it yields 3 : 3-*dimethyl-α-naphthindolinone*,



$$\begin{array}{l}C_6H_4\text{—}C\text{—}NH\\ \;| \qquad\;\; ||\\ CH\colon CH\cdot C\cdot CMe_2\end{array}\!\!>CO$$

which separates from dilute alcohol in white crystals, m. p. 201°, and forms solutions with reddish-blue fluorescence. The *methyl ether*, $C_{15}H_{15}ON$, m. p. 78·5°, is formed by the action of sodium and methyl iodide on the indolinone in methyl-alcoholic solution. The *acetyl* derivative, $C_{16}H_{15}O_2N$, forms a crystalline mass, m. p. 106·5°. With mercuric chloride in concentrated alcoholic or aqueous solution, the indolinone yields a mixture of the *mercurichloride* and the free base; the salt is hydrolysed by excess of water.

iso*Butyryl-β-naphthylhydrazide* is prepared in the same manner as the α-compound. 3 : 3-*Dimethyl-β-naphthindolinone*,



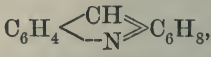
$$C_6H_4<\begin{array}{l}CH\colon C\text{—}NH\\ \qquad\;\; |\\ CH\colon C\cdot CMe_2\end{array}\!\!>CO,$$

forms white crystals, m. p. 145·5°. The *methyl ether*, m. p. 155·5°. The *acetyl* derivative, m. p. 139·5°. G. Y.

Tetrahydroacridine and a New Synthesis of Acridine.

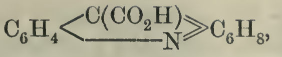
WILHELM BORSCHE [with H. TIEDTKE and W. ROTTSIEPER] (*Ber.*, 1908, **41**, 2203—2208).—The hitherto unknown tetrahydrodibenzopyridines may be prepared by the following three methods: (1) Condensation of α-acyl *cyclo*hexamethylene ketones with aniline and its homologues, and intramolecular condensation of the anilino-compounds initially formed. By this method, a mixture of the isomeric tetrahydroacridine and tetrahydrophenanthridine compound is obtained. (2) Condensation of aromatic *o*-amino-aldehydes or -ketones with hydroaromatic ketones containing a methylene group ortho to the carbonyl group. (3) The hydroaromatic ketone is treated with isatin and strong aqueous alkali, whereby tetrahydroacridine-5-carboxylic acid is formed. The latter, when heated, is converted into tetrahydroacridine with the evolution of carbon dioxide.

[With W. ROTTSIEPER.]—*Tetrahydroacridine*,



$$C_6H_4<\begin{array}{c}CH\\ \text{--}N\end{array}\!\!\geqslant C_6H_8,$$

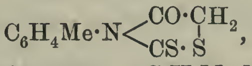
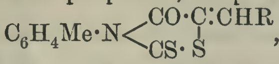
is formed by heating *o*-aminobenzaldehyde with *cyclo*hexanone at 130°, or by treating a solution of these substances in alcohol with a few drops of aqueous sodium hydroxide; it forms small, colourless plates, m. p. 54·5—55°. The *picrate* crystallises in small, yellow needles, m. p. 208—209°; the *methiodide*, $C_{14}H_{16}NI$, is a yellow, crystalline powder, which sinters and then melts at 202—204°; the *platinichloride*, $(C_{13}H_{13}N)_2,H_2PtCl_6$, crystallises in small, brownish-yellow needles, m. p. 233—235°; the *aurichloride*, $(C_{13}H_{13}N)_3,HCl,2HAuCl_4$, is a yellow, crystalline powder, m. p. 156—158°.

Tetrahydroacridine-5-carboxylic acid,  $C_6H_4<\begin{matrix}C(CO_2H)\\ N\end{matrix}\geqslant C_6H_8$, crystallises in small, colourless leaflets, m. p. 284—286° (decomp.); the *hydrochloride,* $C_{14}H_{13}O_2N,HCl$, crystallises in long, colourless needles, m. p. 233°. The *silver, lead,* and *calcium* salts are obtained as white precipitates from aqueous solutions of the *ammonium* salt; the *copper* salt is obtained as a green precipitate.

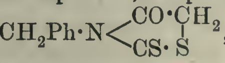
Acridine may be prepared from tetrahydroacridine or its carboxylic acid by distilling with litharge and passing the vapour over heated litharge (compare this vol., i, 365). W. H. G.

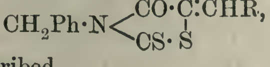
9:10-Phenanthraquinoline. FRIEDRICH HERSCHMANN (*Ber.*, 1908, **41**, 1998—2000).—Skraup's synthesis has for the first time been applied in the phenanthrene series. The interaction of 9-aminophenanthrene, nitrobenzene, glycerol, and concentrated sulphuric acid at 145—150° for four to five hours leads to the formation of a quinoline which must be 9:10-*phenanthraquinoline,* since ring-closure in the 9:8-positions would give a seven-membered ring. The compound forms long, colourless needles, and has m. p. 174°. The *nitrate,* m. p. 240°, *hydrochloride,* m. p. 248°, darkening at 245°, *sulphate, platinichloride,* and *picrate* are mentioned. The reaction with 2-aminophenanthraquinone did not yield a pure product. C. S.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. VII. RUDOLF ANDREASCH (*Monatsh.*, 1908, **29**, 399—419. Compare Abstr., 1907, i, 233).—The substituted rhodanic acids derived from *m*-toluidine, benzylamine, hydrazine, and glycine are now described in amplification of the previous papers on this subject.

3-m-*Tolylrhodanic acid,*  $C_6H_4Me\cdot N<\begin{matrix}CO\cdot CH_2\\ CS\cdot S\end{matrix}$, formed together with *ethyl* m-*tolyldithiocarbaminacetate,* $C_6H_4Me\cdot NH\cdot CS\cdot S\cdot CH_2\cdot CO_2Et$, transparent prisms, m. p. 77°, from ammonium *m*-tolyldithiocarbamate and ethyl chloroacetate, crystallises in microscopic prisms, m. p. 148°. The following *condensation products,*  $C_6H_4Me\cdot N<\begin{matrix}CO\cdot C{:}CHR\\ CS\cdot S\end{matrix}$, of 3-*m*-tolylrhodanic acid with aldehydes are described.

$R = Ph$: yellow needles, m. p. 124°; $R = \cdot C_6H_4\cdot OH$ (*o*): yellow leaflets, becomes red at 190°, m. p. 220°; $R = \cdot C_6H_4\cdot OAc$ (*o*): greyish-white scales, m. p. 231°; $R = \cdot C_6H_4\cdot NO_2$ (*m*): chrome-yellow, microscopic needles, m. p. 234°; $R = \cdot C_6H_4\cdot NMe_2$ (*p*): scarlet, crystalline powder, m. p. 140°, dyes wool, silk, and skin orange-yellow; $R = \cdot C_6H_3{:}O_2{:}CH_2$: chrome-yellow, crystalline powder, m. p. 178°; $R = \cdot CH{:}CHPh$: yellowish-brown powder, m. p. 145—146°.

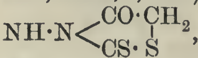
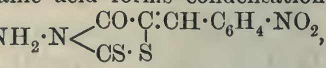
3-*Benzylrhodanic acid,*  $CH_2Ph\cdot N<\begin{matrix}CO\cdot CH_2\\ CS\cdot S\end{matrix}$, prepared from benzylamine, carbon disulphide, and ethyl chloroacetate, crystallises in white leaflets, m. p. 83°. The following condensation *products,*



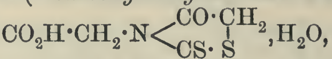
$$CH_2Ph\cdot N<\begin{matrix}CO\cdot C{:}CHR,\\ CS\cdot S\end{matrix}$$

with aldehydes are described.

$R = Ph$: golden needles, m. p. 219°; $R = \cdot C_6H_4\cdot NO_2$ (m): yellow needles, m. p. 183°, becomes superficially colourless on prolonged exposure to light; $R = \cdot C_6H_4\cdot NMe_2$ (p): red needles with blue lustre, m. p. 177°.

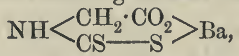
The action of ethyl chloroacetate on hydrazine dithiocarbazate (Curtius and Heidenreich, Abstr., 1894, i, 166) leads to the formation of 3-*aminorhodanic acid*,  $NH\cdot N\left<\begin{matrix}CO\cdot CH_2\\ CS\cdot S\end{matrix}\right.$, which crystallises in slightly yellow needles, m. p. 92°, together with a crystalline *substance*, $C_{10}H_{14}O_4N_2S_3$, m. p. 60°. 3-Aminorhodanic acid forms condensation *products* with *m*-nitrobenzaldehyde,  $NH_2\cdot N\left<\begin{matrix}CO\cdot C{:}CH\cdot C_6H_4\cdot NO_2\\ CS\cdot S\end{matrix}\right.$, yellow needles, m. p. 175—176°, and *p*-dimethylaminobenzaldehyde, $C_3H_2ON_2S_2{:}CH\cdot C_6H_4\cdot NMe_2$, red, microscopic plates, commences to decompose at 200°, m. p. 266°.

Rhodaninacetic acid (3-*carboxymethylrhodanic acid*),

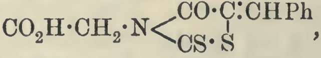


$$CO_2H\cdot CH_2\cdot N\left<\begin{matrix}CO\cdot CH_2\\ CS\cdot S\end{matrix}\right.,H_2O,$$

is formed as the *barium* salt by the action of carbon disulphide and baryta on glycine (compare Siegfried, Abstr., 1905, ii, 332; 1906, i, 324) and treatment of the resulting *barium dithiocarbamate*,



$$NH\left<\begin{matrix}CH_2\cdot CO_2\\ CS\text{——}S\end{matrix}\right>Ba,$$

with ethyl chloroacetate. The rhodaninacetic acid crystallises in needles or leaflets, loses H_2O at 100°, or partially in a vacuum, m. p. 145°, and forms a white *lead* and green *copper* salt; the red *silver* salt rapidly decomposes. The condensation *products* with benzaldehyde,  $CO_2H\cdot CH_2\cdot N\left<\begin{matrix}CO\cdot C{:}CHPh\\ CS\cdot S\end{matrix}\right.$, yellow needles, commence to decompose at 200°, m. p. 240°; *m*-nitrobenzaldehyde, $C_{12}H_8O_3N_2S_2$, yellow needles, commences to decompose at 200°, m. p. 270—280°, and *p*-dimethylaminobenzaldehyde, $C_{14}H_{14}O_3N_2S_2$, orange-red plates, m. p. 235° (decomp.), are described.

Rhodanic acids are obtained also from other amino-acids, such as alanine and aminobenzoic acid; that from asparagine yields a crystalline *benzylidene* derivative. Analogous substances are formed from the hydrolysis products of gelatin and from Witte's peptone. G. Y.

Action of Formaldehyde on Secondary Aromatic Amines. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2145—2156).—When formaldehyde acts on methylaniline or its aliphatic homologues in neutral or alkaline solution, condensation readily occurs with production of derivatives of methylenediamine. In the case of methyl-*o*-toluidine, however, the reaction is more sluggish, and still more so with methyl-*p*-toluidine. On boiling diphenyl-, dimethyl-, or diethyl-methylenediamine with acids or by treating methyl- or ethyl-aniline (2 mols.) with formaldehyde (1 mol.) in acid solution, the product is in each case the same; it consists of a mixture of the original secondary base, the diphenylmethane derivative, and a more complex substance containing about 1½ mols. of the formaldehyde residue to 2 mols. of the base.

The latter is formed in larger amount when a greater excess of formaldehyde is employed; it is formed probably from a further condensation of formaldehyde with the diphenylmethane base, involving the elimination of the hydrogen atom in the ortho-position to the nitrogen and the condensation of a further amount of methylaniline. This explanation is confirmed by the fact that methyl-*o*- and -*p*-toluidines furnish only very small amounts of these complex substances, the diphenylmethane bases derived from them containing only half as many *o*-hydrogen atoms as in the case of that derived from methylaniline.

s-*Diphenyldimethylmethylenediamine*, $CH_2(NPhMe)_2$, prepared from methylaniline and formaldehyde in presence of alkali, forms a mass of white crystals, m. p. 35°. s-*Diphenyldiethylmethylenediamine*, $CH_2(NPhEt)_2$, forms white, glistening needles, m. p. 79°, b. p. 205°/9 mm. *Diethyldiaminodiphenylmethane*, $CH_2(C_6H_4{\cdot}NHEt)_2$, prepared from formaldehyde and ethylaniline in presence of hydrochloric acid, is a pale yellow liquid, b. p. 255°/10 mm.; the *nitroso*-derivative has m. p. 83°, and the *phenylthiocarbamide*, white leaflets, has m. p. 153°. For investigating the action of formaldehyde on methyl-*o*-toluidine, the latter was prepared by the action of cyanogen bromide on dimethyl-*o*-toluidine in the same way as described for methyl-*p*-toluidine (this vol., i, 626). The o-*tolylmethylcyanamide* produced in the reaction has b. p. 135—136°/8 mm., and, on boiling with 30% sulphuric acid for twenty hours, yields methyl-*o*-toluidine and a small amount of dimethyldiaminodi-*o*-tolylmethane. *o*-Tolylcyanamide in contrast to this furnishes *o*-toluidine and *o*-tolylcarbamide.

s-*Di*-o-*tolyldimethylmethylenediamine*, $CH_2(NMe{\cdot}C_6H_4Me)_2$, has b. p. 212—215°/18 mm.; it yields dimethyldiaminodi-*o*-tolylmethane when boiled with acids. s-*Di*-p-*tolyldimethylmethylenediamine* forms white crystals, m. p. 68°. *Dimethyldiaminodi*-p-*tolylmethane* is a tough, gummy substance; the *nitroso*-derivative is a yellow, crystalline powder, m. p. 123°.

The difference exhibited by methylaniline and methyl-*o*-toluidine in their behaviour towards formaldehyde is also shown in the conversion of aminobenzyl bases into diphenylmethane bases by boiling with amines in acid solution. Thus, whilst methyl-*o*-toluidine and dimethylaminobenzyl-*p*-toluidine interact according to the equation

$$NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4Me + C_6H_4Me{\cdot}NHMe = NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_3Me{\cdot}NHMe + NH_2{\cdot}C_6H_4Me,$$

methylaniline furnishes a complex substance similar to that obtained in the formaldehyde condensation, together with *p*-toluidine and *trimethyldiaminodiphenylmethane*, $NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}NHMe$, b. p. 245—246°/9 mm., m. p. 57°, the *nitroso*-derivative of which forms small, yellow crystals, m. p. 96—97°. J. C. C.

Synthesis of *s*-Diphenylcadaverine. [*s*-Diphenylpentamethylenediamine]. JULIUS VON BRAUN (*Ber.*, 1908, 41, 2165—2168).—*s*-Diphenylpentamethylenediamine has been prepared in two ways, namely, (1) aniline is converted by means of αε-dibromo-*n*-pentane into 1-phenylpiperidine, this with cyanogen bromide gives phenyl-ω-bromoamylcyanamide (Abstr., 1907, i, 960), which is condensed with aniline, forming cyanodiphenylpentamethylenediamine, this being hydrolysed finally. (2) Methylaniline is converted into *s*-diphenyldimethylpentamethylenediamine (this vol., i, 678), which is treated with cyanogen bromide, and the resulting *s*-dicyanodiphenylpentamethylenediamine is hydrolysed.

Cyanodiphenylpentamethylenediamine, $CN{\cdot}NPh{\cdot}[CH_2]_5{\cdot}NHPh$, forms small, colourless crystals, m. p. 67°; the *hydrochloride* has m. p. 101°. *Dicyanodiphenylpentamethylenediamine*,

$$CN{\cdot}NPh{\cdot}[CH_2]_5{\cdot}NPh{\cdot}CN,$$

forms white, bushy needles, m. p. 76°. s-*Diphenylpentamethylenediamine*, $NHPh{\cdot}[CH_2]_5{\cdot}NHPh$, has m. p. 45°, b. p. 260—265°/10 mm.; the *hydrochloride*, m. p. 193—194°, the *dibenzoyl* derivative,

$$NPhBz{\cdot}[CH_2]_5{\cdot}NPhBz,$$

hard, glistening crystals, m. p. 124°, and the *dinitroso*-derivative, $NO{\cdot}NPh{\cdot}[CH_2]_5{\cdot}NPh{\cdot}NO$, m. p. 60°, are described. J. C. C.

Coloured Salts of Schiff's Bases. II. Hydrochlorides of Bases formed by Condensing Phenyl-*p*-phenylenediamine with Aromatic Aldehydes. FORRIS J. MOORE and R. G. WOODBRIDGE, JUN. (*J. Amer. Chem. Soc.*, 1908, **30**, 1001—1004).—Moore and Gale (this vol., i, 368) have shown that the bases obtained by condensing *p*-phenylene-*as*-dimethyldiamine with aromatic aldehydes unite with hydrogen chloride in two proportions, forming dark red hydrochlorides and yellow dihydrochlorides.

It is now found that phenyl-*p*-phenylenediamine behaves in a similar manner, but that the dihydrochlorides are formed less readily. All the dihydrochlorides, however, with the exception of that of phenylcinnamylidene-*p*-phenylenediamine, are so stable as to retain their 2 mols. of hydrogen chloride when dried over sodium hydroxide in a vacuous desiccator. The dihydrochloride of the cinnamylidene compound, under these conditions, gradually darkens and loses 1 mol. of hydrogen chloride.

The *mono-* and *di-hydrochlorides* of the following bases have been prepared: benzylidene- and salicylidene-phenyl-*p*-phenylenediamines (Hencke, Abstr., 1889, 609); *phenylpiperonylidene*-p-*phenylenediamine*, m. p. 116°; *phenylanisylidene*-p-*phenylenediamine*, m. p. 105°, which forms silver-grey, pearly scales, and *phenylcinnamylidene*-p-*phenylenediamine*, m. p. 145°, which crystallises in brilliant yellow scales. E. G.

Isomeric Modifications of *p*-Tolildioxime and their Behaviour as to Formation of Complexes. LEO A. TSCHUGAEFF and L. SPIRO (*Ber.*, 1908, **41**, 2219—2221).—The conclusion previously drawn that only the *syn*-forms of 1:2-dioximes give complex metallic compounds with nickel, cobalt, or ferrous salts (this vol., i, 554) is further supported by the behaviour of the *p*-tolildioximes; the *amphi-* and *anti*-compounds give negative results, whereas the *syn*-modifications give with nickel salts a red precipitate, with ammonium palladium chloride and pyridine an orange-red precipitate, and with ferrous sulphate and pyridine a reddish-violet coloration.

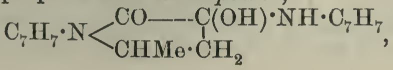
The *syn-* and *anti-p*-tolildioximes have already been prepared by Stierlin (Abstr., 1889, 513); the *amphi*-compound was obtained as follows: On oxidising *p*-tolualdoxime by Beckmann's method (Abstr., 1899, 980), *p-tolualdoxime peroxide*, $(C_6H_4Me\cdot CH{:}N)_2O_2$, is obtained as glistening needles, m. p. 108°. It is insoluble in alkali, and is reduced by ammonium sulphide to aldoxime. By passing nitrous fumes into an ethereal suspension of the peroxide, or, better, into a solution of the aldoxime until almost complete solution of the crystals has occurred, p-*tolildioxime peroxide*, $C_{16}H_{14}O_2N_2$, is obtained, separating from light petroleum in crystals, m. p. 142°. amphi-p-*Tolildioxime*, $C_{16}H_{16}O_2N_2$, obtained by reducing the peroxide in alcoholic solution with zinc dust and acetic acid, forms white needles, which contain 1 mol. of chloroform of crystallisation when this solvent is used. The chloroform-free substance melts on placing it in a bath at 200°, immediately resolidifies, and then has m. p. 229—230°, a phenomenon also characteristic of γ-benzildioxime. It is readily converted into the β-modification at 200°. W. R.

The Benzoylhydrazone of Ethyl *iso*Nitrosoacetoacetate and its Fission Products. CARL BÜLOW and FRITZ SCHAUB (*Ber.*, 1908, **41**, 2181—2183).—When the benzoylhydrazone of ethyl *iso*nitrosoacetoacetate is evaporated with aqueous ammonia or allowed to remain with concentrated sulphuric acid for eight hours, or boiled with alcohol for seventy-one hours, it is decomposed into ethyl alcohol, benzoic acid, and 4-*iso*nitroso-3-methylpyrazolone (compare Knorr, Abstr., 1903, i, 660; Betti, Abstr., 1904, i, 533; Wolff, *ibid.*, 722). The *benzoylhydrazone* of *ethyl* iso*nitrosoacetoacetate*,

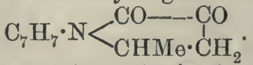
$$NHBz\cdot N{:}CMe\cdot C(N\cdot OH)\cdot CO_2Et,$$

sinters at 164·5°, and is completely decomposed at 173°. The properties of 4-*iso*nitroso-3-methylpyrazolone are correctly given by Betti, and the m. p. is 230—231° (Betti gives 230°). J. C. C.

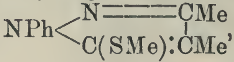
The Mechanism of the Synthesis of Cyclic Nitrogen Compounds [Quinoline Derivatives]. LOUIS J. SIMON (*Compt. rend.*, 1908, **146**, 1400—1402).—In view of the results obtained in the condensation of ethyl oxalacetate with primary amines (Simon and Conduché, Abstr., 1907, i, 963; Simon and Mauguin, this vol., i, 296), the author has repeated his work on the action of pyruvic acid on *p*-toluidine (Abstr., 1898, i, 152) when molecular proportions are mixed in chloroform solution in the cold. The chief product is a very unstable compound, which is readily changed by the action of solvents or heat, or even after some time. This is not *p*-tolilpyruvic acid (*loc. cit.*), but a more complex substance, probably of the constitution $CO_2H\cdot CMe(NH\cdot C_7H_7)\cdot CH_2\cdot C(OH)(NH\cdot C_7H_7)\cdot CO_2H$, which when treated with boiling water yields *p*-toluidine and 2 : 6-*dimethylquinoline-4-carboxylic acid*, decomposing at 265° and furnishing 2 : 6-dimethylquinoline. The *ethyl* ester has m. p. 74°. In the same reaction is also produced a small proportion of a *compound*,

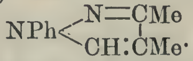


$$C_7H_7\cdot N{<}\begin{matrix}CO\text{——}C(OH)\cdot NH\cdot C_7H_7\\ CHMe\cdot CH_2\end{matrix},$$

which with alcoholic hydrogen chloride gives 1-*tolyl*-2-*methyl*-4 : 5-*diketopyrrolidine*,  $C_7H_7{\cdot}N{<}\begin{array}{l}CO{-}{-}{-}CO\\ CHMe{\cdot}CH_2\end{array}$. The production of these compounds is in accord with the author's views on the mechanism of the synthesis of quinoline derivatives (Abstr., 1907, i, 241). J. C. C.

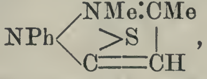
Preparation of 4-Sulphonamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. Emil Scheitlin (D.R.-P. 193632).—4-*Sulphonamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* results from the action of sodium hydrogen sulphite on 4-nitroso-1-phenyl-2 : 3-dimethyl-5-pyrazolone in aqueous solution. It is first produced in the form of its alkali salt, and is precipitated from the aqueous solution of this substance by hydrochloric acid. It is a monobasic acid, and is readily neutralised either by organic bases or alkali carbonates. G. T. M.

Thiopyrazolones. August Michaelis (*Annalen*, 1908, **361**, 251—301).—Since azo-derivatives of thiopyrazolone (Abstr., 1905, i, 392) and of thiopyrines and antipyrines (Abstr., 1901, i, 52; 1904, i, 780) have been described, it seemed of interest to study the parent substances, the thiopyrazolones. Attempts to prepare these by fission of methyl from thiopyrines or ψ-thiopyrines were unsuccessful, as the methyl-sulphur linking is mostly too stable. Whilst antipyrine hydriodide, when heated, decomposes into methyl iodide and phenylmethylpyrazolone, the thiopyrine hydriodides under the same conditions are transformed into the salts of the corresponding ψ-thiopyrines, which are stable towards concentrated hydrochloric acid at 200°. Glacial acetic acid and 48% hydrobromic acid (Stoermer, this vol., i, 190) are also without action. Some ψ-thiopyrines are attacked by hydrogen haloids, but these lose sulphur; thus ψ-methylthiopyrine,  $NPh{<}\begin{array}{l}N{=}{=}{=}CMe\\ C(SMe){:}CMe\end{array}$, forms phenyldimethylpyrazole,



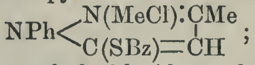
$$NPh{<}\begin{array}{l}N{=}CMe\\ CH{:}CMe\end{array}.$$

It was, however, found possible to prepare 5-thio-1-phenyl-3-methylpyrazolone by the action of benzoyl chloride on thiopyrine,

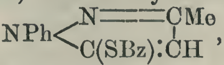
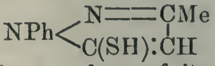


$$NPh\begin{array}{l}\diagup NMe{:}CMe\\ \quad >S \;|\\ \diagdown C{=}{=}CH\end{array},$$

which forms the benzoylthiopyrazolone methochloride,



$$NPh{<}\begin{array}{l}N(MeCl){:}CMe\\ C(SBz){=}CH\end{array};$$

this, when heated, loses methyl chloride, and the resulting benzoylthiopyrazolone,  $NPh{<}\begin{array}{l}N{=}{=}{=}CMe\\ C(SBz){:}CH\end{array}$, on hydrolysis with hydrochloric acid, yields 5-thio-1-phenyl-3-methylpyrazolone,  $NPh{<}\begin{array}{l}N{=}{=}CMe\\ C(SH){:}CH\end{array}$ (Abstr., 1904, i, 780). The derivatives of this thiopyrazolone, of its 4-benzoyl derivative, and of 5-thio-1-*p*-tolyl-3-methylpyrazolone, which has been prepared in the same manner, are now described.

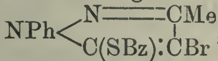
Thiopyrazolones resemble pyrazolones in the following points. They condense with benzaldehyde in molecular proportions, forming benzylidene derivatives. These are colourless in the thiopyrazolone, but intensely red in the pyrazolone, series. Pyrazolones and thiopyrazolones condense with ketones in the molecular proportions 1 : 1 and 1 : 2, in the latter case with loss of hydrogen sulphide and formation of a tricyclic nucleus. Thiopyrazolones, like pyrazolones, form coloured azo-compounds. Both series have basic, as well as acid, properties; the thiopyrazolones are the more strongly acid, and, in correspondence with the great affinity of sulphur for mercury, readily form mercaptides. On the other hand, the thiopyrazolones and pyrazolones show the following differences. With alkyl iodides, the pyrazolones form antipyrines; the thio-compounds, not the corresponding thiopyrines, but ψ-thiopyrines. The azo-compounds of the pyrazolones are antipyrines; those of the thio-series are azo-ψ-thiopyrines. The pyrazolones form stable *iso*nitroso-compounds; the thiopyrazolones, unstable nitroso-compounds, which rapidly change into disulphides. Oxidation of the pyrazolones leads to the formation of bispyrazolones; of the thiopyrazolones, to disulphides or sulphonic acids. On further oxidation, the bispyrazolones form pyrazole-blue, in which two pyrazole nuclei are united by a double linking; the disulphides form colourless compounds, in which two thiopyrazolone groups are united by a sulphur and by a carbon linking.

5-Thio-1-phenyl-3-methylpyrazolone and its Derivatives.—[With ROBERT PANDER.]—The *hydrochloride*, $C_{10}H_{10}N_2S,HCl$, m. p. 145°, *platinichloride*, $(C_{10}H_{10}N_2S)_4,H_4PtCl_8$, yellow powder, m. p. 175°, the *silver* salts, $C_{10}H_9N_2SAg$ and $C_{10}H_9N_2SAg,AgNO_3,H_2O$, the *mercuric* salt, $(C_{10}H_9N_2S)_2Hg$, m. p. 70°, and the *mercurichloride*,

$$C_{10}H_9N_2S,HgCl,$$

white crystals, m. p. 196°, of 5-thio-1-phenyl-3-methylpyrazolone are described. The action of methyl iodide on the thiopyrazolone leads to the formation of ψ-thiopyrine hydriodide.

The benzoyl derivative, m. p. 93° (Abstr., 1904, i, 780), reacts with bromine in glacial acetic acid solution, forming the 4-*bromo*-derivative,



$$\mathrm{NPh}\!<\!\begin{array}{l}\mathrm{N{=\!=}CMe}\\ \quad\quad\quad\;\;|\\ \mathrm{C(SBz){:}CBr}\end{array}$$

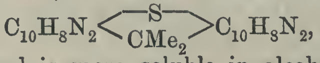
, which crystallises in white needles, m. p. 116°.

The action of benzenesulphonyl chloride on the thiopyrazolone in alkaline solution leads to the formation of the 5-*benzenesulphonylthio*-compound, $C_{10}H_9N_2\cdot S\cdot SO_2Ph$, which is obtained as a yellow oil. With diazobenzene chloride in alkaline solution, the thiopyrazolone forms 5-chloro-1-phenyl-3-methylpyrazole-4-azobenzene (Abstr., 1905, i, 392). When treated with sodium nitrite in acid solution and with iodine in presence of potassium iodide, the thiopyrazolone forms the *disulphide*, $S_2(C_{10}H_9N_2)_2$, which is obtained as a yellow, viscid oil, and gives with platinum tetrachloride a yellow, with mercuric chloride a white, precipitate. On treatment with iodine in alcoholic solution, the thiopyrazolone yields the *disulphide* of an iodo-derivative, $S_2(C_{10}H_8N_2I)_2$, as a white, crystalline precipitate.

1-*Phenyl-3-methylpyrazole-5-sulphonic acid*, $C_{10}H_9N_2\cdot SO_3H$, formed by oxidation of the thiopyrazolone with hydrogen peroxide in very dilute alkaline solution, separates in white crystals, m. p. 235°, and when heated with concentrated hydrochloric acid at 150° is decomposed, forming sulphuric acid and 1-phenyl-3-methylpyrazole. The *sodium*, $C_{10}H_9N_2{\cdot}SO_3Na$, and *barium*, $(+H_2O)$, salts were analysed. On treatment with bromine water, the sulphonic acid yields 4-*bromo*-1-*phenyl*-3-*methylpyrazole*-5-*sulphonic acid*, m. p. 225°, which yields sulphuric acid and 4-bromo-1-phenyl-3-methylpyrazole when heated with an excess of bromine. The *sulphonyl chloride*,

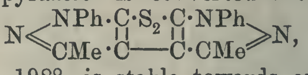
$$C_3N_2HPhMe{\cdot}SO_2Cl,$$

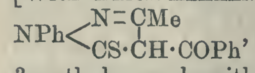
formed by heating the sulphonic acid with phosphorus pentachloride, crystallises in white needles, m. p. 101°, and is hydrolysed by hot water, forming the acid. The *sulphonamide*, $C_{10}H_9N_2{\cdot}SO_2{\cdot}NH_2$, prepared by shaking the sulphonyl chloride with ammonium carbonate, crystallises in white prisms, m. p. 243°, and is soluble in aqueous sodium hydroxide. The *anilide*, $C_{10}H_9N_2{\cdot}SO_2{\cdot}NHPh$, crystallises in needles, m. p. 127°.

The thiopyrazolone reacts with benzaldehyde when heated, forming the 4-*benzylidene* derivative, $C_{10}H_8N_2S{:}CHPh$, which crystallises in white needles, m. p. 183—184°. On prolonged heating, the thiopyrazolone and benzaldehyde yield an amorphous *product*, m. p. 191°. The action of acetone on thiopyrazolone leads to the formation of (*a*) the 4-iso*propylidene* derivative, $C_{10}H_8N_2S{:}CMe_2$, which crystallises in needles, m. p. 204°, is sparingly soluble in alcohol, and when treated with permanganate in acetic acid solution yields a crystalline *substance*, m. p. 150°, and (*b*) a *product*, formed from 2 mols. of the thiopyrazolone and 1 mol. of acetone,  $C_{10}H_8N_2<\substack{-S-\\ CMe_2}>C_{10}H_8N_2$, which forms stout crystals, m. p. 176°, and is more soluble in alcohol and ether than the preceding condensation product. With acetophenone, the thiopyrazolone forms a 4-*phenyl*iso*propylidene* derivative,

$$C_{10}H_8N_2S{:}CPhMe,$$

crystallising in yellow needles, m. p. 135—136°.

When heated with alkalis or concentrated acids, 4-bromo-5-benzoylthio-1-phenyl-3-methyl-4 : 5-dihydropyrazole is converted into *bis*-5-*thio*-1-*phenyl*-3-*methylpyrazolone*,  $N\Big<\substack{NPh{\cdot}C{\cdot}S_2{\cdot}C{\cdot}NPh\\ CMe{\cdot}C{-\!-}C{\cdot}CMe}\Big>N$, which crystallises in white needles, m. p. 198°, is stable towards oxidising and reducing agents, and forms a *methiodide*, $C_{20}H_{16}N_4S_2,MeI$, crystallising in white needles, m. p. 198°, losing methyl iodide.

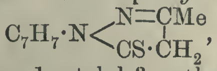
5-Thio-4-benzoyl-1-phenyl-3-methylpyrazolone and its Derivatives.—[With ERICH LEHMANN.]—5-*Thio*-4-*benzoyl*-1-*phenyl*-3-*methylpyrazolone*,  $NPh<\substack{N{=}CMe\\ CS{\cdot}CH{\cdot}COPh}$, prepared by heating 5-chloro-4-benzoyl-1-phenyl-3-methylpyrazole with sodium hydrogen sulphide in alcoholic solution, crystallises in dark yellow needles with red lustre, m. p. 112°, and forms an unstable *hydrochloride*, crystallising in needles. The *mercuric* salt, $(C_{10}H_8N_2SBz)_2Hg$, m. p. 201°, and the *mercurichloride*,

$$C_{10}H_8N_2SBz,HgCl,$$

white needles, m. p. 223°, were analysed. If the 5-chloropyrazole is heated with alcoholic sodium hydrogen sulphide in a sealed tube at 150°, it forms a *substance*, m. p. 174°. When oxidised with hydrogen peroxide in alkaline solution, the thiopyrazolone yields 4-*benzoyl*-1-*phenyl*-3-*methylpyrazole*-5-*sulphonic acid*, which is amorphous, and is hydrolysed by concentrated hydrochloric acid, forming hydrochloric acid and 1-phenyl-4-benzoyl-3-methylpyrazole. One oxidation of the thiopyrazolone with hydrogen peroxide led to the formation of a crystalline *substance*, m. p. 84°. Oxidation of the thiopyrazolone with iodine in alkaline solution leads to the formation of the *disulphide*, $(C_{10}H_8N_2Bz)_2S_2$, which is obtained as a by-product in the preparation of the thiopyrazolone from the 5-chloropyrazole; it crystallises in yellow plates, m. p. 156°, and dissolves in concentrated hydrochloric acid.

5-*Methylthiol*-4-*benzoyl*-1-*phenyl*-3-*methylpyrazole* (4-*benzoyl*-ψ-*thiopyrine*), $COPh\cdot C_3N_2PhMe\cdot SMe$, formed by the action of methyl iodide on the thiopyrazolone in alkaline solution, crystallises in white needles, m. p. 78°, and on oxidation with permanganate in glacial acetic solution yields the *sulphone*, $COPh\cdot C_3N_2PhMe\cdot SO_2Me$, crystallising in colourless plates, m. p. 167°. The 5-*ethylthiol* compound, $COPh\cdot C_3N_2PhMe\cdot SEt$, colourless plates, m. p. 98°, is formed by the action of ethyl iodide on the thiopyrazolone in alkaline solution, or by the action of mercaptan and sodium ethoxide on the 5-chloropyrazole. The *ethylsulphone*, $C_{18}H_{18}O_3N_2S$, crystallises in colourless needles, m. p. 122°. The 5-*phenylthiol* compound, $COPh\cdot C_3N_2PhMe\cdot SPh$, cannot be prepared from the thiopyrazolone, but is obtained by heating the 5-chloropyrazole with thiophenol and sodium ethoxide; it crystallises in colourless needles, m. p. 104°, and yields sulphuric acid when heated with nitric acid only at 300°. The *sulphone*, $C_{23}H_{18}O_3N_2S$, forms colourless needles, m. p. 125°, and when heated with phenylhydrazine is reduced to the phenylthiol compound. The *benzyl ether*, $COPh\cdot C_3N_2PhMe\cdot S\cdot CH_2Ph$, is formed from benzyl chloride and the thiopyrazolone; it crystallises in needles, m. p. 116°. The 5-*benzoyl* derivative, $C_{10}H_8N_2SBz_2$, prepared by shaking the thiopyrazolone with benzoyl chloride in alkaline solution, crystallises in needles, m. p. 107°. The *carboxymethyl ether*, $COPh\cdot C_3N_2PhMe\cdot S\cdot CH_2\cdot CO_2H$, formed from the thiopyrazolone and chloroacetic acid, is obtained in colourless crystals, m. p. 124°, and is soluble in dilute alkalis.

5-*Thio*-1-p-*tolyl*-3-*methylpyrazolone and its Derivatives.*—[With Erich Dulk.]—p-*Tolylthiopyrine*, m. p. 212°, which will be described later, is converted into 5-*benzoylthio*-1-p-*tolyl*-3-*methylpyrazolone*, b. p. 190—200°/15 mm., in the same manner as that employed with the phenyl compound. On hydrolysis with alcoholic potassium hydroxide, the benzoyl compound yields 5-*thio*-1-p-*tolyl*-3-*methylpyrazolone*,



$$C_7H_7\cdot N\Big\langle\begin{matrix}N{=}CMe\\ \vert\\ CS\cdot CH_2\end{matrix},$$

which is also formed from 1-p-tolyl-3-methylpyrazolone by Stoermer and Johannsen's method (Abstr., 1907, i, 966); it is obtained in large, rhombic crystals, m. p. 135°, and behaves towards alkalis and acids in the same manner as the phenyl compound. The *hydrochloride*,

$$C_{11}H_{12}N_2S,HCl,$$

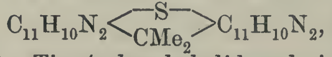
colourless plates; the *mercuric* salt, $(C_{11}H_{11}N_2S)_2Hg$, needles, m. p. 142°; the *mercurichloride*, $C_{11}H_{11}N_2S\cdot HgCl$, prisms, m. p. 208. The *methiodide*, $C_{11}H_{12}N_2S,MeI$, formed by the action of methyl iodide on the thiopyrazole, has m. p. 175°, and is converted by water into the liquid methyl ether. The benzoyl derivative, $C_{11}H_{11}N_2{\cdot}SBz$, crystallises in white needles, m. p. 114°, and forms a 4-*bromo*-derivative, $C_{11}H_{10}N_2Br{\cdot}SBz$, which crystallises in prisms, m. p. 104°, yields benzoic acid and hydrogen bromide when heated with concentrated hydrochloric acid, and appears to form 4-bromo-1-*p*-tolyl-3-methylpyrazolone when treated with alkalis. The *disulphide*, $S_2(C_{11}H_{11}N_2)_2$, forms a yellowish-green mass, m. p. 74°, and is soluble in concentrated hydrochloric acid, being reprecipitated unchanged by water. The 5-*sulphonic acid*, $C_{11}H_{11}N_2{\cdot}SO_3H$, crystallises in white prisms, m. p. 246°; the *barium* salt, $(C_{11}H_{11}O_3N_2S)_2Ba$, forms small prisms. The *sulphonyl chloride*, $C_{11}H_{11}N_2{\cdot}SO_2Cl$, white needles, m. p. 77°. The *sulphonamide*, $C_{11}H_{11}N_2{\cdot}SO_2{\cdot}NH_2$, prisms, m. p. 227°. The *sulphonanilide*,

$$C_{11}H_{11}N_2{\cdot}SO_2{\cdot}NHPh,$$

needles, m. p. 118°.

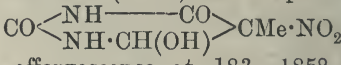
The 4-*benzylidene* derivative, $C_{11}H_{10}N_2S{:}CHPh$, crystallises in white needles, m. p. 212°. When heated with the calculated amount of acetone, the thiopyrazolone yields the 4-iso*propylidene* compound,

$$C_{11}H_{10}N_2S{:}CMe_2,$$

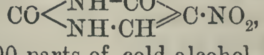
crystallising in colourless needles, m. p. 206°, but if with an excess of acetone and alcohol or a large excess of acetone alone, it forms the condensation *product*,  $C_{11}H_{10}N_2{<}\begin{matrix}—S—\\ CMe_2\end{matrix}{>}C_{11}H_{10}N_2$, which crystallises in needles, m. p. 186°. The 4-*phenylethylidene* derivative,

$$C_{11}H_{10}N_2S{:}CPhMe,$$

formed from the thiopyrazolone and acetophenone, crystallises in colourless needles, m. p. 106°. G. Y.

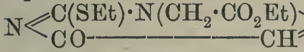
Pyrimidines. VIII. Separation of Thymine from Uracil. TREAT B. JOHNSON (*J. Biol. Chem.*, 1908, 4, 407—418).—When thymine is dissolved in cold fuming nitric acid (D 1·5) and evaporated, crystals of *nitrohydroxyhydrothymine*,  $CO{<}\begin{matrix}NH——CO\\ NH{\cdot}CH(OH)\end{matrix}{>}CMe{\cdot}NO_2$, are formed, which generally melt with effervescence at 183—185° (α-variety), but sometimes at 230—235° (efferv.); on keeping, the latter modification is spontaneously transformed into the former. Both modifications when reduced yield the original thymine.

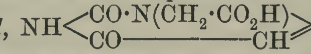
Under the same conditions, uracil yields 5-nitrouracil,

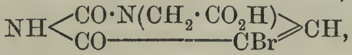


$$CO{<}\begin{matrix}NH-CO\\ NH{\cdot}CH\end{matrix}{\geqslant}C{\cdot}NO_2,$$

which requires 800 to 900 parts of cold alcohol for complete solution, and can be reduced to amino-uracil. Since nitrohydroxyhydrothymine is very soluble in cold alcohol, a separation of the two substances can be readily effected by nitration. One gram of the mixture is dissolved in 10 c.c. of nitric acid (D 1·5); after evaporation of the solution below 60°, the residue is extracted with 15 c.c. of cold alcohol. The nitro-compounds can be purified by crystallisation from hot water and alcohol. C. B.

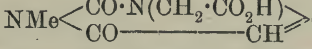
Pyrimidines. XXXI. Synthesis of Uracil-3-acetic Acid. HENRY L. WHEELER and LEONARD M. LIDDLE (*J. Amer. Chem. Soc.*, 1908, 30, 1152—1156).—Johnson and Heyl (Abstr., 1907, i, 728) have found that when 2-ethylthiol-6-pyrimidone is treated with methyl iodide in presence of potassium hydroxide, 2-ethylthiol-1-methyl-6-pyrimidone is produced. When, however, 2-ethylthiol-6-pyrimidone is treated with ethyl chloroacetate and alkali hydroxide, alkylation takes place in the 3-position with formation of *ethyl* 2-*ethylthiol*-6-*pyrimidone*-3-*acetate*,  $\mathrm{N}<\begin{matrix}\mathrm{C(SEt)\cdot N(CH_2\cdot CO_2Et)} \\ \mathrm{CO\text{------------}CH}\end{matrix}>\mathrm{CH}$, m. p. 129°, which crystallises in long, colourless prisms. The corresponding *acid*, m. p. 208—209°, forms slender prisms, and can be prepared either by the hydrolysis of the ester or by heating 2-ethylthiol-6-pyrimidone with potassium chloroacetate. When the acid is warmed with hydrochloric acid, mercaptan is evolved and uracil-3-acetic acid is produced.

Uracil-3-*acetic acid*,  $\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot N(CH_2\cdot CO_2H)} \\ \mathrm{CO\text{------------}CH}\end{matrix}>\mathrm{CH}$, m. p. 285° (decomp.), prepared by heating an alkaline solution of uracil with chloroacetic acid, forms small tablets; its *potassium*, *copper*, and *barium* salts are described. The *methyl* ester melts partly at about 177°, and completely at about 216°. The 5-*bromo*-derivative,



$$\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot N(CH_2\cdot CO_2H)} \\ \mathrm{CO\text{------------}CBr}\end{matrix}>\mathrm{CH},$$

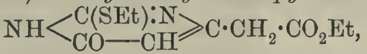
m. p. 244° (decomp.), forms colourless needles. The corresponding 5-*nitro*-derivative, m. p. 264—265° (decomp.), crystallises in colourless prisms.

1-*Methyluracil*-3-*acetic acid*,  $\mathrm{NMe}<\begin{matrix}\mathrm{CO\cdot N(CH_2\cdot CO_2H)} \\ \mathrm{CO\text{------------}CH}\end{matrix}>\mathrm{CH}$, m. p. 239—240°, prepared by the action of potassium chloroacetate on methyluracil or by treating uracil-3-acetic acid with methyl iodide in presence of potassium hydroxide, crystallises in needles or prisms.

E. G.

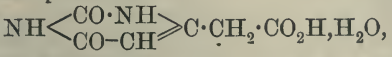
Pyrimidines. XXXII. Synthesis of Uracil-4-acetic Acid.

Henry L. Wheeler and Leonard M. Liddle (*J. Amer. Chem Soc.*, 1908, 30, 1156—1160).—*Ethyl* 2-*ethylthiol*-6-*pyrimidone*-4-*acetate*,

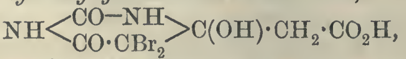


$$\mathrm{NH}<\begin{matrix}\mathrm{C(SEt){:}N} \\ \mathrm{CO\text{---}CH}\end{matrix}>\mathrm{C\cdot CH_2\cdot CO_2Et},$$

m. p. 131°, prepared by the action of ethyl acetonedicarboxylate on an alkaline solution of the ethyl bromide additive product of thiocarbamide, forms long, colourless, silky needles. The corresponding *acid*, m. p. 155° (decomp.), crystallises in colourless needles, and when heated at 170° is converted into 2-ethylthiol-4-methyl-6-pyrimidone. When this acid is warmed with strong hydrochloric acid, mercaptan is evolved and uracil-4-acetic acid is produced.

Uracil-4-*acetic acid*,  $\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot NH} \\ \mathrm{CO{-}CH}\end{matrix}>\mathrm{C\cdot CH_2\cdot CO_2H,H_2O}$, m. p. 340° (decomp.), crystallises in flat prisms and is soluble in about 8 parts of boiling water and in 30 parts of cold water; its *potassium* salt is described. The *ethyl* ester, m. p. 187—189°, crystallises with $1H_2O$. The *methyl* ester has m. p. 216—218°. 5-*Nitrouracil*-4-*acetic acid*, m. p. 153° (decomp.), forms minute cubes.

By the action of bromine on an aqueous solution of uracil-4-acetic acid, 5-*dibromo*-4-*hydroxyhydrouracil*-4-*acetic acid*,



$$\mathrm{NH}\left<\begin{matrix}\mathrm{CO{-}NH}\\ \mathrm{CO\cdot CBr_2}\end{matrix}\right>\mathrm{C(OH)\cdot CH_2\cdot CO_2H},$$

m. p. 240° (decomp.), is produced, which forms colourless plates, probably containing $\frac{1}{2}H_2O$. E. G.

α-Chloro-β-iminazolylpropionic Acid. Adolf Windaus and W. Vogt (*Beitr. chem. Physiol. Path.*, 1908, **11**, 406—408).—By employing the method already given by Fränkel (Abstr., 1906, i, 547) for preparing chlorohistidinecarboxylic acid by treating histidine hydrochloride with nitrous acid and subsequent treatment of the crude product so obtained with zinc dust and glacial acetic acid, the authors have succeeded in obtaining only β-iminazolylpropionic acid. The chlorohistidinecarboxylic acid was, however, obtained by the following method. Histidine was treated with hot potassium nitrate in concentrated hydrochloric acid; the crude hydrochloride of chlorohistidinecarboxylic acid was then esterified by 10% alcoholic hydrogen chloride, and the hydrochloride of the ester thus obtained was precipitated from alcoholic solution by means of ether. This was converted into the oxalate, m. p. 161°. The free ester is an oil, from which, by saponification, pure chlorohistidinecarboxylic acid can be obtained. This melts at 191° (decomp.).

β-Iminazolylpropionic acid, on the other hand, which agrees in properties with the substance described by Fränkel as chlorohistidinecarboxylic acid, has m. p. 80°, and when heated loses H_2O.

S. B. S.

Hydroxyquinoxalines. Otto Hinsberg (*Ber.*, 1908, **41**, 2031—2033).—Five compounds, $C_8H_6O_2N_2$, have been prepared; these have been termed: 1. Dihydroxyquinoxaline (Bladin, Abstr., 1885, 785); 2. Dihydroxyethylenephenylenediamine (Aschan, *ibid.*, 1886, 147); 3. Dihydroxyquinoxaline (Hinsberg and Pollak, *ibid.*, 1896, i, 394); 4. Phenyleneoxamide (Seeliger and Meyer, *ibid.*, 1897, i, 45); 5. Phenyleneoxamide (Motylowski, this vol., i, 371). Compounds 2 to 5 are shown to be identical. Although compounds 1 and 3 were previously stated to be identical, it is now shown that they are different substances. Hinsberg and Pollak's compound, unlike Bladin's, does not combine with water of crystallisation.

Motylowski's oxidation product of hydroxydihydroquinoxaline is probably identical with 2-hydroxyquinoxaline. J. J. S.

Synthesis of Phenylquinoxalines. Otto Fischer and Fritz Römer (*Ber.*, 1908, **41**, 2350—2353).—Fischer and Schindler described recently (this vol., i, 221) the formation of 2- and 3-phenylnaphthaquinoxalines from diketo-*s*-αβ-naphthazine and diketo-*as*-αβ-naphthazine respectively. As these phenylnaphthaquinoxalines were previously unknown, and in their properties differed markedly from Feist and Arnstein's phenylnaphthaquinoxaline prepared from β-naphthaquinone and phenylethylenediamine (Abstr., 1895, i, 258), it was advisable to confirm their constitution by synthesis. For this purpose, the authors employed Hinsberg's method for the preparation of phenylquinoxalines from bromoacetophenone and *o*-diamines, and found that the action of bromoacetophenone on 1 : 2-diaminonaphthalene leads to the formation of the two products described by Fischer and Schindler, but in small yields and accompanied by much resin. Better yields are obtained by employing *iso*nitrosoacetophenone, which reacts more smoothly than does bromoacetophenone with *o*-diamines, and with *o*-phenylenediamine gives good yields of phenylquinoxaline (Hinsberg, Abstr., 1897, i, 120).

Fischer and Schindler's phenylnaphthaquinoxalines are formed when *iso*nitrosoacetophenone and 1 : 2-diaminonaphthalene are boiled in molecular proportions in methyl-alcoholic solution. The 2-phenyl-compound is now found to be white. Both quinoxalines are volatile with steam, and give with zinc dust and acetic acid a transient red coloration. If boiled in ethyl-alcoholic solution, *iso*nitrosoacetophenone and 1 : 2-diaminonaphthalene form, together with the quinoxalines, a *substance*, which separates from pyridine in red crystals, and gives green and blue colorations with concentrated sulphuric acid. This red substance is not formed in presence of small amounts of hydroxylamine hydrochloride.

The repetition of Feist and Arnstein's experiment shows that these authors could not have obtained a single substance. The action of ethylenediamine, which oxidises more easily than phenylethylenediamine, on β-naphthaquinone leads to the formation of naphthaquinoxaline (Hinsberg, Abstr., 1890, 972). The *picrate*, $C_{18}H_{11}O_7N_5$, crystallises in yellow needles, m. p. 171°. G. Y.

Preparation of Isatin and its Methyl Derivative. RUDOLPH BAUER (D.R.-P. 193633).—It has been found that isatin and its methyl derivatives can be produced by the action of warm concentrated sulphuric acid on substituted iminochlorides having the general formula $RN{:}CCl{\cdot}CCl{:}NR$, where R is a phenyl or tolyl group. Diphenyloxaliminochloride, m. p. 115°, di-*o*-tolyloxaliminochloride, m. p. 131°, *di*-m-*tolyloxaliminochloride*, yellow prisms, m. p. 72°, and *di*-p-*tolyloxaliminochloride*, yellow leaflets, m. p. 107°, were employed in this synthesis. *o*-Methylisatin, which is fully described for the first time, yields a *phenylhydrazone*, golden needles, m. p. 242°, and *oxime*, yellow needles, m. p. 235°. G. T. M.

Preparation of Stable Chloroindigotins. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 193971).—A stable chloroindigotin, $C_{16}H_9O_2N_2Cl$, is obtained by passing chlorine into a mixture of finely-powdered indigotin and nitrobenzene. A vigorous reaction occurs, and the chloro-derivative is produced in a crystalline form. When reduced with alkaline hyposulphite, this substance furnishes a light yellow leuco-derivative, which has valuable tinctorial properties. G. T. M.

Preparation of Halogen Derivatives of β-Naphthindigotin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 193970).—*Bromo-β-naphthindigotin* is prepared by successively brominating β-naphthisatin, converting the bromo-derivative into the chloride, reducing the latter with hydriodic acid or some other suitable reducing agent, and finally oxidising the product with air in the presence of sodium hydroxide. The product is a dark green, crystalline powder, which furnishes a reddish-brown leuco-derivative giving fast shades of blue on cotton. G. T. M.

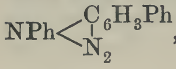
Transformation of *s*-Phenyldiphenylhydrazine by Hydrogen Chloride in Benzene Solution.

MIECISLAS DZIURZYŃSKI (*Bull. Acad. Sci. Cracow*, 1908, 401—408).—When *s*-phenyldiphenylhydrazine is dissolved in benzene and the solution saturated with hydrogen chloride, intramolecular change takes place with formation of a semidine base and a diphenyline base, which are separated by means of their different solubilities in aqueous alcohol.

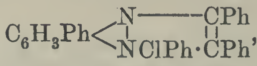
The semidine base, which is probably 3-*amino*-4-*anilinodiphenyl*,

$$NHPh\cdot C_6H_3(NH_2)\cdot C_6H_5,$$

crystallises in silvery scales, m. p. 141°. The *acetyl* derivative forms white needles, m. p. 165°. The *hydrochloride* and the *sulphate* are described. With nitrous acid, the base yields an *azimino*-derivative,

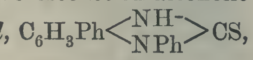


$NPh<\begin{array}{l}C_6H_3Ph\\ \mid\\ N_2\end{array}$, m. p. 82·5°, with benzil a *compound*,



$$C_6H_3Ph<\begin{array}{l}N\text{———}CPh\\ \mid\qquad\quad\ \ \|\\ NClPh\cdot CPh\end{array},$$

of which the free *base* gives a yellowish-green fluorescence in alcoholic solution, and with carbon disulphide a *compound*,



$C_6H_3Ph<\begin{array}{l}NH\text{-}\\ NPh\end{array}>CS$,

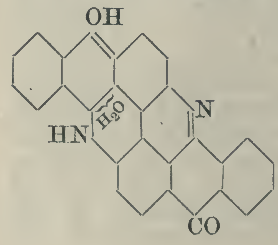
yellowish-white scales, m. p. 150°.

The diphenyline base, which is probably 2 : 4′-*diamino*-p-*diphenylbenzene*, $NH_2\cdot C_6H_3Ph\cdot C_6H_4\cdot NH_2$, is a dark oil, crystallising after some months. The *diacetyl* derivative forms small, hard crystals, m. p. 223°. The *dihydrochloride* is blue, and the *sulphate* crystallises from alcohol in white needles. In the filtrate from the precipitated bases, 4-benzeneazodiphenyl was recognised. J. C. C.

Indanthren and Flavanthren, X. Products of Reduction of Flavanthren and the Relation between their Colour and Constitution.

ROLAND SCHOLL (*Ber.*, 1908, 41, 2304—2328. Compare Abstr., 1907, i, 540).—By the reduction of flavanthren, the author has prepared seven compounds, namely, dihydroflavanthren, α- and β-tetrahydroflavanthrens, α- and β-hexahydroflavanthrens, flavanthrine, and flavanthrinol, of which the fourth and the last will be described in a later paper.

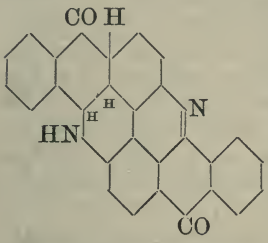
[With KARL HOLDERMANN.]—*Dihydroflavanthren hydrate* is prepared by reducing flavanthrene with alkaline sodium hyposulphite in an atmosphere of hydrogen. On cooling, bronzy needles of the *disodium* salt (annexed formula, in which the OH and H_2O groups are replaced by ONa and NaOH respectively) crystallise out, and are treated with acetic acid. Dark bluish-green, coppery crystals are obtained, which are fairly stable at the ordinary temperature, but are readily oxidised to flavanthren at 100°, or when moist; when heated for a few hours at 150—170° in a stream of carbon dioxide, water is lost and *dihydroflavanthren* is formed. This

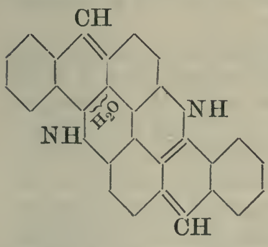


is a green powder, which is not so readily oxidised by the air as is the hydrate. It is also the chief product when flavanthren is heated with hydriodic acid and red phosphorus at 125°. Although flavanthren is of a very weakly basic character, dihydroflavanthren hydrate readily forms salts with mineral acids. *Dihydroflavanthren hydrochloride* probably contains the acid united with the nitrogen atom.

o-*Benzoyldihydroflavanthren* is a reddish-brown powder, m. p. 220° (decomp.).

a-Tetrahydroflavanthren hydrate could not be isolated, but the *sodium* salt is stated to be formed when flavanthren is reduced by zinc dust and sodium hydroxide. On acidification, a mixture of dihydroflavanthren hydrate with a small amount of a-hexahydroflavanthren hydrate results. *β-Tetrahydroflavanthren* (annexed formula), prepared by treating flavanthren with hydriodic acid and red phosphorus at 170°, is a green powder. It forms salts with acids and alkalis, in the latter case passing into the red enolic modification. The *dibenzoyl* derivative forms microscopic, lemon-yellow prisms. The authors consider that β-hexahydroflavanthren is formed when the red alkaline solution of β-tetrahydroflavanthren is reduced with zinc dust, but the compound could not be isolated from the resulting yellow solution. By reducing flavanthren with hydriodic acid and red phosphorus at 207—210°, *flavanthrine hydrate*, annexed formula, is formed as a greenish-brown powder, which on heating to 240° loses water and yields *flavanthrine*. This forms large, brown needles with a green, metallic lustre, and sinters at 380°, m. p. about 390°. It is readily oxidised to flavanthren.





The relation between the colour and constitution of these reduction products of flavanthren is discussed.

J. C. C.

Influence of Methyl Groups on the Tinctorial Properties of the Basic Dyes derived from Triphenylmethane. JEAN BIELECKI and ALEXANDRE KOLENIEW (*Bull. Acad. Sci. Cracow*, 1908, 296—318).—It is well known that the presence of such substituents as SO_3H, Cl, Br, NO_2, OH, and CO_2H in the ortho-position to the methane-carbon atom of basic triphenylmethane dyes belonging to the malachite-green and magenta series renders them more resistant towards alkalis. The authors have now examined the effect of introducing the methyl group, not only in the ortho-position (where any increased fastness to alkalis might be assigned to steric hindrance of the change of the quinonoid to the carbinol structure under the influence of alkalis), but also in the meta- and para-positions to the methane carbon-atom. It is found that, in all three positions, the presence of the methyl group increases the fastness to alkalis, whilst with regard to the shade produced, its influence is similar to that exerted by the acidic groups cited above; in the meta-position no change in colour is evident, whilst in the ortho- and para-positions the change is marked; thus *o*-methylated malachite-green is bluish-green and the *p*-methylated derivative is yellowish-green.

The dyes were prepared by condensing tetramethyldiaminodiphenylcarbinol with 1 mol. of an amine (mostly homologues of dimethylaniline). When the operation is effected in presence of dilute hydrochloric acid, the amine usually attaches itself to the methane-carbon atom at the position para to the amino-group, but when concentrated sulphuric acid is used, the point of union is in the meta-position (compare Noelting, Abstr., 1892, 187).

4-*Amino*-4′ : 4″-*tetramethyldiaminodiphenyl*-o-*tolylmethane*,

$$CH(C_6H_4\cdot NMe_2)_2\cdot C_6H_3Me\cdot NH_2,$$

prepared by condensing the carbinol with *o*-toluidine in dilute hydrochloric acid, has m. p. 184°, and is readily oxidised to a *dye*, which dyes tannin-mordanted cotton in violet-blue shades. When sulphuric acid is used as condensing agent, there is formed 3-*amino*-4′ : 4″-*tetramethyldiaminodiphenyl*-o-*tolylmethane*, m. p. 146°, which on oxidation yields a green *dye*. 4 : 4′ : 4″-*Hexamethyltriaminodiphenyl*-o-*tolylmethane*, prepared from dimethyl-*o*-toluidine by condensing it with the carbinol in dilute hydrochloric acid, separates from ether as a pale yellow, microcrystalline powder, m. p. 144°. On oxidation, it yields a violet-blue *dye*. When sulphuric acid is used as the condensing agent, 3 : 4′ : 4″-*hexamethyltriaminodiphenyl*-o-*toluidine*, m. p. 113°, is obtained, which on oxidation gives a yellowish-green *dye*.

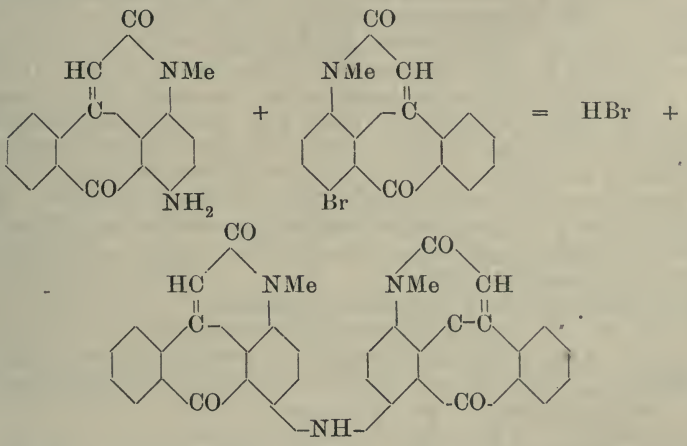
4 : 4′ : 4″-*Hexamethyltriaminodiphenyl*-m-*tolylmethane* is prepared by condensing the carbinol with dimethyl-*m*-toluidine in presence of either dilute hydrochloric or concentrated sulphuric acid. It crystallises from methyl alcohol in colourless prisms, m. p. 118°, and on oxidation yields a violet-blue *dye*. 2 : 4′ : 4″-*Hexamethyltriaminodiphenyl*-p-*tolylmethane*, prepared from the carbinol, dimethyl-*p*-toluidine, and dilute hydrochloric acid, crystallises from methyl alcohol in pale yellow flocks, m. p. 107°. The corresponding *dye* is violet-blue. When 100% sulphuric acid is used as the condensing agent, 3 : 4′ : 4″-hexamethyltriaminodiphenyl-*p*-tolylmethane, white prisms, m. p. 113°, is obtained (Noelting, Abstr., 1892, 190, gives 100°). The corresponding dye is bluish-green (compare L. Cassella & Co., Abstr., 1904, i, 804).

2 : 4′ : 4″-*Hexamethyltriaminodiphenyl*-m-*xylylmethane*, prepared by condensing the carbinol with dimethyl-*m*-4-xylidine in dilute hydrochloric acid, crystallises from methyl alcohol in yellow flocks, m. p. 115°. The corresponding *dye* is blue. When 100% sulphuric acid is the condensing agent, 3 : 4′ : 4″-*hexamethyltriaminodiphenyl*-m-*xylylmethane*, prisms, m. p. 135°, is obtained. The corresponding *dye* is greenish-blue. 4 : 4′ : 4″-*Hexamethyltriaminodiphenyl*-p-*xylylmethane* is prepared from the carbinol and dimethyl-*p*-xylidine by the aid of either dilute hydrochloric or 100% sulphuric acid. It crystallises from methyl alcohol in long needles, m. p. 150°. The corresponding *dye* is violet-blue. 2 : 4′ : 4″-*Hexamethyltriminodiphenyl*-o-*xylylmethane*, prepared from the carbinol and dimethyl-*o*-4-xylidine in presence of dilute hydrochloric acid, has m. p. 164°. This base could not be oxidised

either by tetrachloro-*p*-benzoquinone or lead peroxide. 3 : 4′ : 4″-*Hexamethyltriaminodiphenyl*-o-*xylylmethane* is obtained when 100% sulphuric acid is used as the condensing agent in the preceding reaction. It crystallises from methyl alcohol in leaflets, m. p. 185°. The corresponding *dye* is deep blue. J. C. C.

Preparation of Anthracene Derivatives Containing Nitrogen.

Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 194253. Compare this vol., i, 456).—By condensing 1 : 4-aminoanthrapyridone with 4-bromoanthrapyridone by means of dry sodium acetate and copper chloride in the presence of naphthalene, a compound crystallising in dark violet needles is obtained, which is formed in accordance with the following equation :



A similar compound containing one anthrapyridone and one anthraquinone residue is obtained by condensing 1 : 4-bromoanthrapyridone and 4-aminoanthraquinone. Several substances of the same type are described in the patent. G. T. M.

Constitution and Colour.

Friedrich Kehrmann (*Ber.*, 1908, 41, 2340—2345).—Partly a criticism of Willstätter and Piccard's views as to the constitution of Wurster's dyes (this vol., i, 475). The author shows that change of colour can take place in two ways, namely, (1) without change in constitution of the chromophoric group: this occurs when an auxochromic group is introduced; and (2) accompanied by change in constitution of the chromophore, as when colourless bases yield coloured salts and *vice versâ*. Quinhydrones are more strongly coloured than quinones, owing to the presence of the auxochromic hydroxyl group, and the compounds to which Willstätter and Piccard have assigned a special constitution do not differ in kind, but only in degree, from ordinary quinhydrones, and are therefore to be regarded as having a constitution similar to these. J. C. C.

Dihydrazines. I. 4:4′-Bismethylhydrazinodiphenylmethane, a Reagent for the Characterisation of Aldehydes. Julius von Braun (*Ber.*, 1908, **41**, 2169—2181).—4 : 4′-Bismethylhydrazinodiphenylmethane, obtained by reducing dinitrosodimethyldiaminodiphenylmethane (Braun and Kayser, Abstr., 1904, i, 687) with zinc and acetic acid, reacts instantly with alphyl and aryl aldehydes, forming condensation products which are readily characterised. It reacts very slowly with ketones, so that a convenient method is afforded of distinguishing between the two. An exception to this rule is displayed by α-keto-carboxylic acids, which react as if they were aldehydes. Aldehydic sugars, such as mannose and galactose, condense immediately, but dextrose reacts only very slowly.

4 : 4′-*Bismethylhydrazinodiphenylmethane*, $CH_2(C_6H_4\cdot NMe\cdot NH_2)_2$, has m. p. 102°; the *hydrochloride*, m. p. 190° (decomp.), and *sulphate* are described. The *semicarbazide*, $CH_2(C_6H_4\cdot NMe\cdot NH\cdot CO\cdot NH_2)_2$, is a white powder, m. p. 232°; the *phenylthiosemicarbazide* has m. p. 211°, and the *benzoyl* derivative softens at 176° and has m. p. 181°.

4 : 4′-Bismethylhydrazinodiphenylmethane condenses to hydrazones of the type $CH_2(C_6H_4\cdot NMe\cdot N\colon CH\cdot R)_2$ with the following aldehydes, the figures in brackets being the m. p.: formaldehyde (137°), acetaldehyde (114°), butaldehyde (71°), heptaldehyde (57°), citral (107—108°), benzaldehyde (220°, softening at 214°), cuminaldehyde (169°), anisaldehyde (195°), p-dimethylaminobenzaldehyde (209°), salicylaldehyde (200° with previous sintering), opianic acid (220°), cinnamaldehyde (203°), furfuraldehyde (201°).

Acetophenone yields a deep yellow *compound*,

$$CH_2(C_6H_4\cdot NMe\cdot N\colon CPhMe)_2,$$

m. p. 105°; the *compound* from benzophenone is deep yellow, sintering at 120°, m. p. 152°; glyoxal yields a *compound*, $C_{17}H_{18}N_4$, decomp. 280—282°, and methylglyoxal the *compound*,

$$CH_2(C_6H_4\cdot NMe\cdot N\colon CH\cdot COMe)_2,$$

m. p. 185°. Pyruvic acid gives a yellow *compound*,

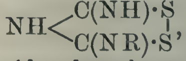
$$CH_2(C_6H_4\cdot NMe\cdot N\colon CMe\cdot CO_2H)_2,$$

m. p. 100° (decomp.), and phenylpyruvic acid behaves similarly. Phthalonic acid, the *phenylmethylhydrazone* of which is yellow and has m. p. 140° (decomp.), gives a *compound*,

$$CH_2[C_6H_4\cdot NMe\cdot N\colon C(CO_2H)\cdot C_6H_4\cdot CO_2H]_2,$$

softening at 60°, m. p. 78°, and decomposing at 90°. J. C. C.

Disulphides with Neighbouring Double Linkings. III. Emil Fromm (*Annalen*, 1908, **361**, 302—352. Compare Abstr., 1906, i, 656, 714; 1907, i, 982).—It has been shown that all disulphides with neighbouring double linkings, $X\colon CR\cdot S\cdot S\cdot C\colon Y$, are decomposed by alkalis and amines with liberation of sulphur and formation of new compounds. Thus perthiocyanic acid reacts with phenylhydrazine, forming sulphur, phenyldithiourazole, 3-amino-5-thion-1-phenyldihydrotriazole, and anilthiuret. Similarly, the thiurets,



$NH<\begin{matrix}C(NH)\cdot S\\ C(NR)\cdot S\end{matrix}$,

react with phenylhydrazine, forming two products, considered to have the formulæ $NHR\cdot CS\cdot NH\cdot C(NH)\cdot NH\cdot NHPh$ and

$$NHR\cdot CS\cdot NH\cdot C(NH)\cdot NPh\cdot NH_2.$$

Fromm and Vetter (Abstr., 1907, i, 982) obtained only one product from the interaction of aniline and phenylthiuret, which was considered to have the formula $NHPh\cdot CS\cdot NH\cdot C(NH)\cdot NHPh$. In continuing the investigation, it has now been found that the action of aromatic amines on thiurets gives rise to two products; thus, with aniline and *p*-tolylthiuret, there are formed phenylguanido-*p*-tolylthiocarbamide, $C_7H_7\cdot N\colon C(SH)\cdot NH\cdot C(NH)\cdot NHPh$, and phenyl-*p*-tolylguanidothiocarbamide, $C_7H_7\cdot N\colon C(NHPh)\cdot NH\cdot C(SH)\colon NH$.

The action of aniline or phenylhydrazine on thiurets, which are derived from secondary amines, is found to lead to the substitution of the anilino- or phenylhydrazino-group for the secondary amine residue.

The phenyldithiourazole described by Fromm and Schneider (Abstr., 1906, i, 714) has been re-studied, and in connexion with it a number of new dithiobiurets and their derivatives have been prepared.

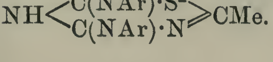
Action of Aromatic Amines and Hydrazines on p-*Tolylthiuret*.—[With Arnold Weller.]—p-*Tolylthiuret hydrochloride*, $C_9H_{10}N_3S_2Cl$, is formed by boiling *p*-tolyldithiobiuret with ferric chloride and hydrochloric acid; it is obtained as a yellow, amorphous powder, m. p. 194°, and, when boiled with 2 mols. of aniline in alcoholic solution, forms two products: (*a*) *Phenylguanido*-p-*tolylthiocarbamide*, $C_{15}H_{16}N_4S$, separates from the hot alcoholic solution and crystallises in white leaflets, m. p. 182°. Its *hydrochloride*, $C_{15}H_{16}N_4S,HCl$, forms white needles, m. p. 214° (? 244°). (*b*) *Phenyl*-p-*tolylguanidothiocarbamide* is isolated from the alcoholic filtrate as the *hydrochloride*, $C_{15}H_{16}N_4S,HCl$, which crystallises in needles, m. p. 158°. When boiled with benzyl chloride and alcoholic sodium hydroxide, the base from (*a*) yields *phenylguanido*-p-*tolyl*-ψ-*benzylthiocarbamide*, $C_{22}H_{11}N_4S$, which crystallises in white leaflets, m. p. 176°, whereas, under the same conditions, the base from (*b*) is converted into *phenyl*-p-*tolyldicyanodiamide*, which crystallises in white leaflets, m. p. 186°.

The action of *p*-toluidine on phenylthiuret leads to formation of only one product, which is identical with the phenyl-*p*-tolylguanidothiocarbamide described above.

p-*Tolylguanido*-p-*tolylthiocarbamide*, $C_{16}H_{18}N_4S$, formed by the action of *p*-toluidine on *p*-tolylthiuret, crystallises in white needles, m. p. 170—180°; the ψ-*benzyl* derivative forms yellow needles, m. p. 199°.

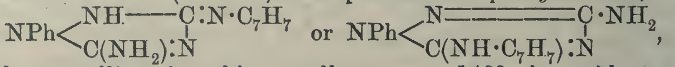
The arylguanidoarylthiocarbamides are readily acetylised by means of acetic anhydride, whilst the diarylguanidothiocarbamides, on the other hand, do not form acetyl derivatives.

Acetylphenylguanido-p-*tolylthiocarbamide*, $C_{17}H_{18}ON_4S$, crystallises in needles, m. p. 225°. When it is heated with sodium hydroxide and benzyl chloride, the latter does not enter into reaction, but the alkali converts the acetyl compound into an *anhydro*-derivative, $C_{17}H_{16}N_4S$, which crystallises in white needles, m. p. 185°, and when heated with concentrated aqueous sodium hydroxide yields acetic acid and phenylguanido-*p*-tolylthiocarbamide. *Acetyl*-p-*tolylguanido*-p-*tolylthiocarbamide*, $C_{18}H_{20}ON_4S$, crystallises in white needles, m. p. 194°. The *anhydro*-derivative, $C_{18}H_{18}N_4S$, forms needles, m. p. 206°. It is considered that these anhydro-derivatives have the constitution



$$NH<\begin{matrix}C(NAr)\cdot S-\\ C(NAr)\cdot N=\end{matrix}>CMe.$$

Action of Phenylhydrazine on p-*Tolylthiuret.*—When treated with 2 mols. of phenylhydrazine, *p*-tolylthiuret hydrochloride yields *amino-phenylguanido*-p-*tolylthiocarbamide*, $NH_2{\cdot}NPh{\cdot}C(NC_7H_7){\cdot}NH{\cdot}C(SH){:}NH$ or $NH_2{\cdot}NPh{\cdot}C(NH){\cdot}NH{\cdot}C(NC_7H_7){\cdot}SH$, which crystallises in white leaflets, m. p. 168°, and forms a *benzylidene* derivative, $C_{22}H_{21}N_5S$, greenish-yellow powder, decomp. 110°. Alcoholic sodium hydroxide converts aminophenylguanido-p-tolylthiocarbamide into 3 : 5-(or 5 : 3-)*amino*-p-*toluidino*-1-*phenyltriazole*,



$$NPh{<}\begin{matrix}NH\text{———}C{:}N{\cdot}C_7H_7\\ C(NH_2){:}N\end{matrix}\quad\text{or}\quad NPh{<}\begin{matrix}N\text{========}C{\cdot}NH_2\\ C(NH{\cdot}C_7H_7){:}N\end{matrix},$$

which crystallises in white needles, m. p. 148°, is stable towards boiling acids or alkalis, and forms crystalline salts with acids. The *hydrochloride*, $C_{15}H_{15}N_5,HCl$, white needles, m. p. 172°. The *acetyl* derivative, $C_{17}H_{17}ON_5$, m. p. 115°.

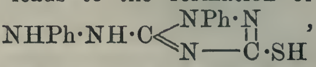
Action of Aromatic Amines and Hydrazines on Phenylmethylthiuret and Phenylethylthiuret.—[With H. Baumhauer.]—*Phenylethyldithiobiuret*, $C_{10}H_{13}N_3S_2$, formed by heating perthiocyanic acid with ethylaniline, separates from alcohol in crystals, m. p. 119·5°, and when boiled with dilute hydrochloric acid and ferric chloride yields *phenylethylthiuret hydrochloride*, $C_{10}H_{11}N_3S_2,HCl$, m. p. 230°.

When boiled with aniline in alcoholic solution, phenyl-, methyl-, or phenylethyl-thiuret yields phenylguanidophenylthiocarbamide, sulphur, and methyl- or ethyl-aniline. Methylphenylthiuret reacts with methylaniline at 120—125°, forming sulphur and the *compound*,

$$C(NPhMe)_2{\cdot}NH{\cdot}CS{\cdot}NH_2,$$

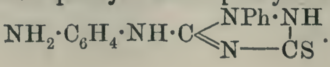
m. p. 90°, which cannot be benzylated with benzyl chloride and sodium hydroxide, but forms lead sulphide when heated with sodium plumbate.

When boiled with 2 mols. of phenylhydrazine, phenylmethylthiuret yields sulphur, methylaniline, 3-amino-5-thiol-1-phenyltriazole, m. p. 234°, and *dianildithiobiuret*, $NH(CS{\cdot}NH{\cdot}NHPh)_2$, which crystallises from alcohol in needles, m. p. 178°. The action of cold potassium hydroxide solution on dianildithiobiuret leads to the formation of 3-*thiol*-5-*phenylhydrazino*-1-*phenyltriazole*,



$$NHPh{\cdot}NH{\cdot}C{<}\begin{matrix}NPh{\cdot}N\\ N\text{——}C{\cdot}SH\end{matrix},$$

which forms yellowish-red crystals, m. p. 177°, and is oxidised by sulphur in boiling alkaline, or by iodine in boiling alcoholic, solution, forming the *benzeneazotriazole*, $NPh{:}N{\cdot}C_2N_3Ph{\cdot}SH$, which is obtained in brownish-red crystals, m. p. 218°, and is soluble in aqueous alkalis. The action of acetic anhydride on dianildithiobiuret leads to the formation of a *substance*, which has m. p. 218°, but is not identical with the preceding azo-compound, as when boiled with aqueous potassium hydroxide and reprecipitated by an acid it yields the hydrazino-compound, m. p. 177°. When boiled with hydrochloric acid, dianildithiobiuret yields the preceding azo-compound, m. p. 218°, and a *base*, $C_{14}H_{13}N_5S$, which crystallises in white needles, m. p. 180·5°, and is probably 3-thio-1-phenyl-5-aminophenylaminotriazole,



$$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}C{<}\begin{matrix}NPh{\cdot}NH\\ N\text{——}CS\end{matrix}.$$

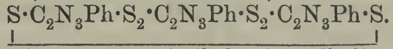
This forms a diacetyl derivative, $C_{18}H_{17}O_2N_5S$, crystallising in colourless needles, m. p. 106°, and a *dibenzylidene* derivative, $C_{28}H_{21}N_5S$, m. p. 195°.

The action of phenylhydrazine on phenylmethyldithiobiuret in boiling alcoholic solution leads to the formation of 3-amino-5-thiol-1-phenyltriazole, m. p. 244°, and 3 : 5-dithiol-1-phenyltriazole, m. p. 193°.

Oxidation Products of 3 : 5-*Dithiol*-1-*phenyltriazole.*—[With H. Baumhauer.]—The oxidation of 3 : 5-dithiol-1-phenyltriazole by means of iodine in alcoholic solution leads to the formation of two products: the one, m. p. 181°, previously (Abstr., 1906, i, 714) given as $C_{16}H_{10}N_6S_4$, is now considered to be

$$SH\cdot C_2N_3Ph\cdot S_2\cdot C_2N_3Ph\cdot S_2\cdot C_2N_3Ph\cdot SH;$$

the other, m. p. 163°, has the constitution,



$$S\cdot C_2N_3Ph\cdot S_2\cdot C_2N_3Ph\cdot S_2\cdot C_2N_3Ph\cdot S.$$

Both oxidation products, when boiled with alkalis, yield the parent dithiolphenyltriazole and small amounts of 3-(or 5-)*thiol*-1-*phenyltriazole*, $C_2N_3H_2SPh$, which crystallises in colourless needles, m. p. 178°, and forms a *benzyl* derivative, $C_{15}H_{13}N_3S$, m. p. 64°.

New Dithiobiurets and their Derivatives.—[With A. Weller.]—*β-Naphthyldithiobiuret*, $C_{12}H_{11}N_3S_2$, formed from perthiocyanic acid and β-naphthylamine, is obtained as a white powder, m. p. 245°.

Dimethylaminophenyldithiobiuret hydrochloride, $C_{10}H_{14}N_4S_2,HCl$, formed from perthiocyanic acid and aminodimethylaniline, crystallises in white needles, m. p. 205°. The free *base* forms yellow needles, m. p. 168—169°.

β-Naphthylthiuret hydrochloride, $C_{12}H_{10}N_3S_2Cl$, formed by boiling the dithiobiuret with ferric chloride and hydrochloric acid, separates from dilute hydrochloric acid in crystals, m. p. above 300°. *Dimethylaminophenylthiuret hydriodide*, $C_{10}H_{12}N_4S_2,2HI,C_2H_6O$, formed by adding iodine to the dithiobiuret in alcoholic solution, crystallises in yellow needles, decomp. 175°.

Formation of Cyanoamides.—The action of benzyl chloride and sodium hydroxide on dithiobiurets leads to the formation of cyano-ψ-benzylthiocarbamides. *Cyano-β-naphthyl-ψ-benzylthiocarbamide*,

$$C_{10}H_7\cdot N{:}C(S\cdot CH_2Ph)\cdot NH\cdot CN,$$

crystallises in white leaflets, m. p. 201°. *Cyanodimethylaminophenyl-ψ-benzylthiocarbamide*, $C_{17}H_{18}N_4S$, formed from dimethylaminophenyldithiobiuret, crystallises in white needles, m. p. 193°. Cyano-*p*-tolyl-ψ-benzylthiocarbamide (Abstr., 1906, i, 656) is now found to be formed when *p*-tolyldithiobiuret is heated with benzyl chloride and concentrated ammonia added. G. Y.

Preparation of Hydroxyalkyl Derivatives of Xanthine Bases.

Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 193799. Compare this vol., i, 475).—The xanthine bases condense with alkylene oxides to form hydroxyalkyl derivatives. 1 : 3-Dimethyl-7-hydroxyethylxanthine is thus obtained by heating theophylline and ethylene oxide at 130°. Dehydrating agents, such as zinc or hydrogen chloride, may be employed, and theobromine, 3-methylxanthine, and other bases may be similarly condensed with propylene and trimethylene oxides.

G. T. M.

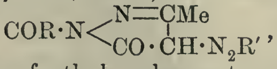
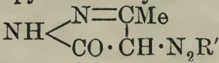
Physico-chemical Researches on the Behaviour of Urates in Solution. F. Gudzent (*Zeitsch. physiol. Chem.*, 1908, **56**, 150—179).—Urates, in which both acidic hydrogen atoms are replaced by a metal, are hydrolysed in solution to monatomic salts; of these, monosodium urate crystallises with $1H_2O$, and monopotassium and monoammonium urate crystallise anhydrous. On continued shaking, the amount of these salts dissolved passes through a maximum, and then diminishes somewhat, this ultimate diminution being 4—5 times greater for the ammonium salt than for the sodium and potassium salts. The diminution is not explicable, and is not due to hydrolysis or to a change in size of the particles, or to hydration of the excess of solid salt with which the solution is shaken. The maximum solubilities are: 1 part of potassium, of sodium, and of ammonium urate requires respectively at 18°, 653, 1201, and 2415, and at 37°, 370, 665, and 1352 parts of water. G. B.

Position of Entrance of the Diazo-group in the Formation of Azo-dyes. Wassili Scharwin and Kaljanoff (*Ber.*, 1908, **41**, 2056—2060).—The rule that the diazo-group enters the ortho-position in a para-substituted amine or phenol does not always hold good. Thus, when the auxochrome is a dialkylamino-group, either no combination takes place (probably owing to stearic hindrance) or the *p*-substituent is displaced with formation of the corresponding dye. The authors show that when *p*-diazobenzenesulphonic acid acts on dimethyl-*p*-toluidine, *p*-bromodimethylaniline, dimethylsulphanilic acid, *p*-dimethylaminodiphenylmethane, tetramethylbenzidine, or *N*-dimethyl-β-naphthylamine, no dye is formed. *N*-Dimethyl-α-naphthylamine, as was to be expected, forms 4-p-*sulphobenzeneazo*-1-*dimethylnaphthylamine*, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot NMe_2$, crystallising from water in violet, glistening needles. The *sodium* salt forms golden-yellow leaflets. The authors confirm Pinnow's observation (Abstr., 1895, i, 98) that helianthin is formed when diazobenzenesulphonic acid acts on tetramethyldiaminodiphenylmethane, and show that the reaction proceeds according to the equation

$$2SO_3H\cdot C_6H_4\cdot N_2\cdot OH + NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2 = 2SO_3H\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe_2 + CH_2O + H_2O.$$

A similar reaction takes place when *p*-nitrodiazobenzene is used (compare Noelting, Abstr., 1888, 270; Bamberger, Abstr., 1895, i, 351).

When diazobenzenesulphonic acid acts on *p*-dimethylaminobenzoic acid, the carboxyl group is eliminated and helianthin is formed (compare Limpricht, Abstr., 1891, 1036) without any other product (compare Grandmougin and Freimann, Abstr., 1907, i, 986). By treating *m*-phenylenetetramethyldiamine with diazobenzenesulphonic acid, 4-*p*-sulphobenzeneazo-*m*-phenylenetetramethyldiamine (Pinnow and Wegner, Abstr., 1898, i, 185) was prepared. This forms microscopic, Bordeaux-red needles; the *alkali* salts are orange-coloured. J. C. C.

Ethyl Arylazoacetoacetateacylhydrazones and their Conversion into Derivatives of 4-Arylazo-3-methyl-5-pyrazolones with an Acid Radicle Attached to the Primary Nitrogen Atom. Carl Bülow and Friedrich Schaub (*Ber.*, 1908, **41**, 2355—2366. Compare Abstr., 1907, i, 301; this vol., i, 579; Curtius, Darapsky, and Müller, Abstr., 1907, i, 451).—A number of 4-arylazo-1-acyl-3-methylpyrazolones,  $\mathrm{COR{\cdot}N}\Big<\begin{matrix}\mathrm{N{=}CMe}\\ \mathrm{CO{\cdot}CH{\cdot}N_2R'}\end{matrix}$, have been prepared from 1:2-acylhydrazones of ethyl arylazoacetoacetates, $\mathrm{COR{\cdot}NH{\cdot}N{:}CMe{\cdot}CH(N_2R'){\cdot}CO_2Et}$. Contrary to the statements of Curtius and Struve (Abstr., 1895, i, 34), therefore, pyrazolones can be formed from the acylhydrazones of α-substituted ethyl acetoacetates. On hydrolysis, the acyl-pyrazolone yields the corresponding 4-arylazo-3-methyl-5-pyrazolone,  $\mathrm{NH}\Big<\begin{matrix}\mathrm{N{=}CMe}\\ \mathrm{CO{\cdot}CH{\cdot}N_2R'}\end{matrix}$, which can be synthesised from the ethyl arylazoacetoacetates, $\mathrm{COMe{\cdot}CH(N_2R'){\cdot}CO_2Et}$.

The benzoylhydrazones of ethyl arylazoacetoacetates are formed from the ethyl arylazoacetoacetate and benzoylhydrazide in cooled acetic acid solution, and can be recrystallised only under certain conditions, as intramolecular ring condensation, followed in some cases by fission of the benzoyl group, takes place with great ease.

The *benzoylhydrazone* of ethyl phenylazoacetoacetate, $C_{19}H_{20}O_3N_4$, crystallises in canary-yellow needles, m. p. 156°, and, when dissolved in cold dilute alkali hydroxides and precipitated immediately by means of carbon dioxide, is regained unchanged. When heated with aqueous sodium hydroxide or acetate on the water-bath, it condenses to 4-benzeneazo-3-methyl-5-pyrazolone, $C_{10}H_{10}ON_4$, which crystallises in orange-red leaflets, m. p. 199·5—200° (197°: Rothenburg, 1895, i, 686).

Ethyl o-*tolylazoacetoacetate*, $C_{13}H_{12}O_3N_2$, formed by the action of diazotised *o*-toluidine on ethyl acetoacetate in presence of sodium acetate, crystallises in lemon-yellow needles, m. p. 67°. The *benzoylhydrazone* crystallises in yellow needles, m. p. 145—149°, and on recrystallisation forms 4-o-*tolueneazo*-3-*methylpyrazolone*, $C_{11}H_{12}ON_4$, orange leaflets, m. p. 224—225°, and its 1-*benzoyl* derivative, $C_{18}H_{16}O_2N_4$, scales, m. p. 209°.

The *benzoyl* derivative of ethyl *p*-tolylazoacetoacetate, formed from diazotised *p*-toluidine and ethyl acetoacetate, crystallises in yellow needles, m. p. 165°. 4-p-*Tolueneazo*-3-*methyl*-5-*pyrazolone* forms orange leaflets, m. p. 196°.

Ethyl m-*xylylazoacetoacetate*, $C_{14}H_{18}O_3N_2$, crystallises in yellow needles, m. p. 121°. The *benzoylhydrazone*, $C_{21}H_{24}O_3N_4$, m. p. 145—149°. 4-m-*Xyleneazo*-1-*benzoyl*-3-*methyl*-5-*pyrazolone*, $C_{19}H_{18}O_2N_4$, orange-red needles, m. p. 171—172°. 4-m-*Xyleneazo*-3-*methyl*-5-*pyrazolone*, $C_{12}H_{14}ON_4$, m. p. 190—191°.

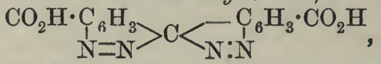
The *benzoylhydrazone* of ethyl α-naphthylazoacetoacetate, $C_{23}H_{22}O_3N_4$, forms brownish-yellow threads, m. p. 165—167° (decomp.). 4-α-*Naphthaleneazo*-1-*benzoyl*-3-*methyl*-5-*pyrazolone*, $C_{21}H_{16}O_2N_4$, yellowish-red needles, m. p. 212°. 4-α-*Naphthaleneazo*-3-*methyl*-5-*pyrazolone*, $C_{14}H_{12}ON_4$, brownish-red crystals, m. p. 247°.

The *benzoylhydrazone* of ethyl β-naphthylazoacetoacetate, $C_{23}H_{22}O_3N_4$, forms canary-yellow crystals, m. p. 160—164° (decomp.). 4-β-*Naphthaleneazo*-1-*benzoyl*-3-*methyl*-5-*pyrazolone*, $C_{21}H_{16}O_2N_4$, orange crystals, m. p. 224°. 4-β-*Naphthaleneazo*-3-*methyl*-5-*pyrazolone* forms red crystals, m. p. 237—238°, and yields a *sodium* salt, which is decomposed by carbon dioxide or boiling alcohol.

Ethyl carboxyphenylazoacetoacetate, $C_{13}H_{14}O_5N_2$, formed from diazotised anthranilic acid, is obtained in yellow crystals, m. p. 162—163°. The *benzoylhydrazone*, yellow crystals, m. p. 244—245°. 4-*Carboxybenzeneazo-3-methyl-5-pyrazolone*, $C_{11}H_{10}O_3N_4$, crystallises in orange needles, m. p. above 280° (decomp.). G. Y.

Bisazo-compounds. HENRI DUVAL (*Compt. rend.*, 1908, **146**, 1407—1409).—Continuing his recent work (Abstr., 1907, i, 663), the author finds that nitrous acid acts on the di-*o*-amino-derivatives of diphenylmethane-4 : 4′-dicarboxylic acid, of 4 : 4′-dicyanodiphenylmethane, and of 4 : 4′-diacetyldiphenylmethane to produce bisazo-compounds, whilst with the di-*o*-amino-derivatives of diphenylmethane and of 4 : 4′-diacetyldiaminodiphenylmethane, nitrous acid gives a mixture of the corresponding phenol and the bisazo-compound.

Bisazodiphenylmethane-4 : 4′-*dicarboxylic acid*,



$$\begin{matrix} CO_2H\cdot C_6H_3 & & —C_6H_3\cdot CO_2H \\ | & >C< & | \\ N{=}N & & N{:}N \end{matrix},$$

can be obtained by hydrolysing its ethyl ester (*loc. cit.*), but is best prepared as described above. It melts above 300°. 4 : 4′-*Dicyanobisazodiphenylmethane* melts above 350°. 4 : 4′-*Diacetylbisazodiphenylmethane* separates from pyridine in bright yellow crystals, decomp. at about 300°. 4 : 4′-*Diacetyldiaminobisazodiphenylmethane* forms red crystals, m. p. above 300°. The conclusion is drawn that the presence of an electronegative substituent in the diphenylmethane nucleus favours the formation of bisazo-compounds of the above type.

J. C. C.

Aminoazo-compounds. ARTHUR HANTZSCH (*Ber.*, 1908, **41**, 2435—2437).—Reply to Hewitt (this vol., i, 581). C. S.

Protein Constitution. New Method of Hydrolysis by Means of Hydrofluoric Acid. L. HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1908, **146**, 1291—1293).—It is claimed that hydrofluoric acid is superior to other acids as a reagent for the hydrolysis of proteins. Far less of the humin substances are formed; the acid can be readily removed after completion of the reaction by calcium carbonate, and the amino- and diamino-acids formed can be obtained in a state of great purity. Commercial hydrofluoric acid (50%) diluted with about five times its volume of water is employed. The mixture with proteins is heated in lead vessels on a water-bath for from forty-eight to one hundred hours, until the biuret reaction disappears. S. B. S.

Calorimetric Investigation on Protein Precipitation. AMEDEO HERLITZKA (*Biochem. Zeitsch.*, 1908, **11**, 481—492).—During the process of salting-out protein with ammonium sulphate, or during the converse process of re-solution due to dilution, there is no development of heat. In the precipitation process, only protein, and not any salt, is precipitated. In precipitation with silver nitrate, the precipitate contains both protein and silver, and heat is developed. If, however, the precipitate contains much silver, heat production is negative, due to adsorption of silver by the protein. The heat developed is 4·18 calories per gram of protein. If adsorption occurs, the calorific value is – 16·67 cal. per gram of silver nitrate. W. D. H.

The Diffusion of Colloids. II. Reginald O. Herzog and H. Kasarnowski (*Biochem. Zeitsch.*, 1908, **11**, 172—176).—The diffusion coefficients of various colloidal substances were determined. The coefficient can be regarded as a physical constant. By its means it can be determined whether a given product is a mixture; trypsin, for example, was found to consist of a mixture of ferments. By means of the diffusion constant, from the equation $M=59{\cdot}2/K^2$, the molecular weight of a solution can be determined.

The results agree well with those obtained by other methods. For ovalbumin, the molecular weight found was 17,000; for ovomucoid, 30,000; for pepsin, 13,000; for invertin, 54,000, and for emulsin, 45,000. S. B. S.

The Influence of Temperature on the Co-aggregation of Colloids. Bertram H. Buxton and Alfred H. Rahe (*Beitr. chem. Physiol. Path.*, 1908, **11**, 479—501).—The different colloids were mixed with dye solutions, chiefly night-blue and Janus-green, and the concentration was noted at which co-aggregation of the colloids most readily took place at temperatures between 0° and 80°. In the case of negative organic colloids, it was found that the higher the temperature the greater the quantity of dye necessary to produce co-aggregation. The increased quantities necessary when the temperature is raised are much greater in the case of reversible colloids than in that of irreversible colloids. These phenomena are absent in the case of inorganic colloids.

When basic hydroxides are used to produce co-aggregation of negative organic colloids, instead of dyes, the quantity is independent of temperature. Mastic appears to be an exception to this rule.

Experiments were also made by transferring the mixtures, after the co-aggregation phenomena had been observed at a particular temperature, to higher and lower temperatures, with the object of studying reversion of the phenomena. By increasing the temperature, it was found that the type that was characteristic at the lower temperature was converted into the type characteristic for the higher. Lowering the temperature did not, however, alter the type. S. B. S.

Changes in the Physical State of Colloids. VI. Compounds of Salt Ions with Amphoteric Protein. Wolfgang Pauli and Hans Handovsky (*Beitr. chem. Physiol. Path.*, 1908, **11**, 415—448).—By amphoteric protein is meant protein which has been subjected to so long a period of dialysis that the product is no longer a salt of either acid or base. For the purposes of the investigation, ox-serum was employed, which had been dialysed against repeatedly-changed carbon dioxide-free water for at least six weeks. To determine the influence of salts on such a protein, the coagulation-temperature was ascertained in the presence of varying quantities. It was found that both the ions and anions had influence on the coagulation-temperature. The chlorides of potassium, sodium, ammonium, and magnesium give curves of similar form (when the concentrations are plotted as abscissæ, and the coagulation-temperatures as ordinates), which rise at first rapidly and then slowly. The curves given by the alkaline-earth chlorides show a maximum coagulation-temperature when the concentration of the salt reaches $N/2$; after this point there is a fall. The curve for lithium chloride lies between those of the two groups, showing a maximum coagulation point only when the concentration reaches $1N$. The influence of the different anions is very varied. The potassium salts were used in the experiments. Cl, Br, SO_4, and NO_3 form a group in which additions of salt up to concentrations of 0·5 to $1N$ cause a rise of coagulation-temperature; additions beyond this point up to 1 to $3N$ cause but slight variations. SCN and I act in a similar way up to 0·5 to $1N$; above this point they cause marked inhibition, and potassium thiocyanate in $1N$ solution and potassium iodide in $2N$ solution cause total inhibition.

The inhibition of coagulation can be due to two causes; either a change in the protein, such as the formation of an acid or alkali albumin, or an inhibition of the aggregation of charged particles. To test this point, a protein solution containing potassium thiocyanate in concentration $2N$ was boiled for some minutes, and then divided into two portions; one was kept under toluene, and the other was dialysed; the former remained clear, and the latter gradually deposited coagulated protein. The experiment indicates that the coagulation is inhibited by the salt preventing the aggregation of particles.

It was assumed that proteins in salt solutions form adsorption compounds with salts, and that the formation of such compounds exerts a marked influence on the coagulation-temperature. If this is the case, then $t - t_0 = Kc^m$, where K and m are constants, c the concentration of the salt, and t and t_0 the coagulation-temperatures of protein salt mixture and pure protein solutions respectively. If $\log(t - t_0)$ be plotted as ordinates and $\log c$ as abscissæ, the curve representing the relations between the temperature of coagulation and concentration of the salt should be a straight line. This was the case with several of the salts investigated (up to concentrations of $0·1N$). At higher concentrations, other more complex factors come into play.

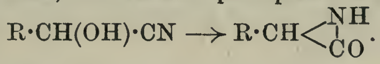
The theory of surface adsorption of salt ions by proteins was further tested by the measurement of viscosities. Protein, even in small concentration, considerably increases the internal friction of water, whereas inorganic salts up to concentrations of $0·05N$ have but little influence. If the theory of surface adsorption is correct, the salt ions on the surface of the colloidal protein molecules should mask the influence of the latter on the internal friction. It was found that neutral salts, which by themselves increase the viscosity of pure water, without exception lower the internal friction of amphoteric protein; in fact, in presence of sodium chloride, thiocyanate, and sulphate, calcium chloride, and potassium thiocyanate in concentrations of 0·01 to $0·05N$ (in which concentrations of the salts alone the viscosity of water is increased), the viscosity of the protein is lower than that of pure protein solution.

Non-electrolytes, such as sucrose, have but little influence on the coagulation-temperature; they have but little influence also on the internal friction of protein solutions. The case of urea is somewhat exceptional. This substance appears to act chemically on the proteins. The general parallelism between the influence of substances on heat coagulation and internal friction of protein supports generally a conception of adsorption compounds.

The action of alkalis and readily hydrolysed salts, such as aluminium chloride, was investigated. In these cases the conditions are much more complex. S. B. S.

The Formation of Hydrogen Sulphide from Protein and Sulphur. HERMANN HILDEBRANDT (*Beitr. chem. Physiol. Path.*, 1908, **11**, 409—410).—Experiments made by precipitating proteins with tannic acid and with mercuric chloride show that the substances which cause precipitation do not always prevent the reducing action of proteins on sulphur. A protein which has been precipitated with tannic acid can cause the reduction of sulphur, whereas one which has been precipitated with mercuric chloride has lost this property. S. B. S.

Complete Hydrolytic Decomposition of Egg-albumin at 180°. P. W. LATHAM (*Biochem. J.*, 1908, **3**, 207—240). **The Synthesis of Living Albumin.** P. W. LATHAM (*Biochem. J.*, 1908, **3**, 241—257).—Two theoretical papers, consisting of speculations based on the old results of Schützenberger, but without any new experimental facts. It is pointed out how the leucéines and a number of other substances obtained by Schützenberger might be synthesised (in the laboratory) from pyruvic acid. In accordance with Pflüger's view, the death of protoplasm is regarded as consisting in the change



$R{\cdot}CH(OH){\cdot}CN \longrightarrow R{\cdot}CH{<}\begin{matrix}NH\\ |\\ CO\end{matrix}$. G. B.

A Modification of the Properties of Gluten produced by Sulphurous Acid. J. DUGAST (*Compt. rend.*, 1908, **146**, 1287—1288).—Gluten undergoes a considerable change in its physical properties when treated with sulphurous acid; flour which has been submitted to the fumes of the acid, on this account, loses its value for bread-making. S. B. S.

Action of Reducing Agents on Compounds of Hæmoglobin. BEINTKER (*Chem. Zentr.*, 1908, i, 1630; from *Vrtljschr. ger. Med. öffentl. Sanitätswesen.*, 1908, **35**, 262—265).—Experiments have been made with ammonium sulphide, sodium hypophosphite, sodium hydrogen sulphite, hydroxylamine hydrochloride, hydrogen sulphide, ferrous tartrate in ammoniacal solution, and stannous chloride. It is found that sodium hydrogen sulphite is as good a reducing agent for blood as hydrogen sulphide or ferrous tartrate, and has the advantage that it does not greatly increase the quantity of blood and gives a clear, colourless solution. J. V. E.

Hæmopyrrole. LEON MARCHLEWSKI and J. RETINGER (*Biochem. Zeitsch.*, 1908, 10, 437—453).—The hæmopyrrole obtained by the reduction of hæmatoporphyrin appears, according to the later researches of Küster, to be a mixture of substances. He succeeded in obtaining by oxidation an imide which was not that of methylpropylmaleic acid, but corresponded more with that of methylmaleic acid. The analyses of the product obtained by the action of diazobenzene chloride on hæmopyrrole (Marchlewski, Goldmann, and Hetper) indicated that hæmopyrrole is a methylpropyl rather than a methylethyl derivative of pyrrole. Further investigations of the action of diazobenzene chloride on hæmopyrrole have revealed the fact that the product just discussed, with the formula $C_{20}H_{22}N_5Cl$, is accompanied by another crystalline product of ruby red colour, a substance crystallising in green needles, and a third product crystallising in reddish-violet needles. S. B. S.

The Carbohydrate Group in Nucleic Acid. II. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1908, 56, 212—219. Compare this vol., i, 487).—The proofs that nucleic acid yields a pentose are regarded as insufficient; on theoretical grounds, the carbohydrate is more probably a hexose, and this is supported by experiment. W. D. H.

State of Combination of Sulphur in the Keratin Molecule. OSKAR BAUDISCH (*Chem. Zeit.*, 1908, 32, 620).—With the object of obtaining evidence that the sulphur is in combination with oxygen in the keratin molecule, the author has repeated the experiments of Raikow (Abstr., 1905, i, 725), using wool, and substantiated his results that syrupy phosphoric acid at the ordinary temperature oxidises the sulphur contained to sulphur dioxide. Further, the oxidation of the sulphur of the wool to sulphur trioxide has been effected at the ordinary temperature by means of hydrogen peroxide. When, however, the wool is first chlorinated, no trace of sulphur dioxide is observed when treated with phosphoric acid. J. V. E.

Phenomena of the "Precipitation" and "Insolubilisation" of Gelatin. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1908, [iv], 3, 743—750. Compare Abstr., 1907, i, 573).—The action of a large number of organic and inorganic substances on gelatin solutions has been examined with a view to ascertaining (1) whether those substances which "precipitate" gelatin or render it "insoluble" have any characters in common, and (2) the nature of the "precipitated" and "insolubilised" gelatins formed.

It is found that in the "precipitation" reactions, two types of products are formed: (*a*) substances soluble in warm water, which have the properties and composition of the original gelatin; (*b*) substances insoluble in warm water, in which the properties of the original gelatin have been considerably modified. The first type of product is obtained when (1) concentrated solutions of alkali salts, (2) dilute solutions of phosphotungstic or phosphomolybdic acid, and (3) phenols or substitution products of phenols are added to solutions of gelatin. The second type of product is obtained when substances capable of furnishing oxygen, directly or indirectly, are added to gelatin solutions, for example, the halogens, ferric salts, uranates, manganates, permanganates, &c. Among organic substances, tannin is the only substance which gives with gelatin a precipitate insoluble in warm water.

Gelatin is "rendered insoluble" but not "precipitated" by chromium salts, and by formaldehyde, quinone, and oxidation products of various polyhydric phenols (compare Abstr., 1906, i, 614, 915, 999; 1907, i, 573).
T. A. H.

Gelatoses. ZDENKO H. SKRAUP and F. HUMMELBERGER (*Monatsh.*, 1908, **29**, 451—469).—The hydrolysis of proteins with the object of obtaining albumoses and peptones is usually carried out by means of enzymes or very dilute acids. The authors have now studied the hydrolysis by means of relatively concentrated acid, and have endeavoured to improve the ammonium sulphate method of separating the products. Gelatin was chosen for study in consequence of its solubility in water and acids. The fractions precipitated from the product of hydrolysis by concentrated acid by means of various concentrations of ammonium sulphate were isolated and hydrolysed. Glycine, glutamic acid, arginine, and lysine, which occur in glutin in large amounts, and histidine were estimated in the product of the hydrolysis of each fraction; other amino-acids, which occur only in small amounts, were not estimated. On complete hydrolysis, gelatin yields the following percentages of cleavage products: glutamic acid, 13·9, estimated by Horbaczewski's method, or 10·1, estimated by Fischer's esterification method; glycine, 9·6, 9·7; histidine, 0·4; arginine, 6·2; lysine, 4·4. Fischer found only 0·9% of glutamic acid, but 16·5% of glycine, and Levene (Abstr., 1907, i, 168), 16·38% of glycine from gelatin.

Whilst gelatin is hydrolysed completely to simple amino-acids by boiling 25% sulphuric acid (Levene, *loc. cit.*), products of partial hydrolysis are obtained with the same acid at 50°. The albumoses, precipitated on partial and on complete saturation of the hydrolysis product with ammonium sulphate, and the peptone fraction, which is soluble in ammonium sulphate and was purified by dialysis, were hydrolysed by boiling concentrated hydrochloric acid, or by boiling dilute hydrochloric acid and stannous chloride. The albumoses precipitated by one-third or by one-half saturation gave the following percentages, *A*, of cleavage products; those precipitated by complete saturation gave the percentages *B*; the peptone solution gave the percentages *C*; and the first solution from the dialysator, the percentages *D*.

	Glutamic acid.						
	Fischer's method.	Horbaczewski's method.	Glycine.		Histidine.	Arginine.	Lysine.
A	2·5	5·8	10·2	10·3	5·8		1·8
B	15	11	6·6	10·5	5·4		2·3
C	20·8		7·2		0·4	6·3	3·8
D	16		4·1		0·3	4·0	4·8

The more soluble the albumose in ammonium sulphate solution the greater its percentage of glutamic acid and histidine, but the smaller the percentage of glycine. The peptone is distinguished from the albumoses by a high percentage of glutamic acid and small percentage of glycine. G. Y.

Preparation of Stable Soluble Compounds of Hexamethylenetetramine Silver Nitrate with Albumoses. ALBERT BUSCH (D.R.-P. 193740).—Hexamethylenetetramine silver nitrate combines with albumoses in aqueous solution to form a soluble additive compound containing 8 per cent. of silver, which is obtained as a yellowish-brown powder either on concentrating the solution under reduced pressure or by precipitation with alcohol.

The dry components may also be mixed, and an extract made with 50% alcohol; the product is then obtained by evaporating down this solution. G. T. M.

Studies on Enzyme Action. XI. Hydrolysis of Raffinose by Acids and Enzymes. HENRY E. ARMSTRONG and WILLIAM H. GLOVER (*Proc. Roy. Soc.*, 1908, 80, *B*, 312—321).—The rate of hydrolysis of raffinose into melibiose and lævulose, both by invertase and by acids, was investigated, and compared with the rate of action of the same reagents on sucrose. The rate of hydrolysis of raffinose is considerably smaller than that of sucrose. The influence of the stereochemical configuration on the rate of hydrolysis is discussed.

S. B. S.

Physico-chemical Investigation of Amylase and Maltase. MLLE. CH. PHILOCHE (*J. Chim. Phys.*, 1908, 6, 355—423. Compare this vol., ii, 470).—*Action of Amylase on Starch and Glycogen* (continued).—In a solution containing 0·004% of amylase of malt and 2% of starch, hydrolysis is practically complete in eight to nine hours, and even for smaller enzyme concentrations there does not appear to be any interruption of the reaction. On the other hand, a 2% solution of glycogen is completely hydrolysed by a 2% solution of amylase of malt only after twenty-six hours, and in solutions containing less than 1% of the enzyme hydrolysis is incomplete. For solutions containing 0·01 to 0·125% of the enzyme, the proportion of maltose formed is approximately proportional to the enzyme concentration. The stoppage of the reaction is not due to the destruction or weakening of the enzyme, and in such partly hydrolysed solutions the glycogen is no longer present in its original form.

Glycogen is hydrolysed somewhat less rapidly than starch by pancreatic juice, but, as shown above, amylase acts much less rapidly on glycogen than on starch. The rate of reaction between amylase and starch is somewhat complicated; it diminishes fairly rapidly until about 30% of the starch is decomposed, and then proceeds as a unimolecular reaction until hydrolysis is almost complete.

The last part of the paper contains a general discussion of the mechanism of enzyme reactions in the light of all the available accurate data. The reactions take place in heterogeneous systems, and the purely chemical actions are therefore complicated by diffusion and adsorption phenomena (compare Nernst, Abstr., 1904, ii, 315; Henri, Abstr., 1906, ii, 13). G. S.

Organic Chemistry.

Action of Metallic Oxides on the Primary Alcohols (Irreducible Oxides). Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1908, **147**, 106—110. Compare this vol., i, 594).—Many metallic oxides, which are not reduced by alcohol vapour, decompose primary alcohols catalytically. The decomposition may be into hydrogen and an aldehyde, as with manganous oxide (and also with stannous and cadmium oxides; these two are, however, slowly reduced); secondly, the decomposition may be a dehydration, alumina, thoria, and blue oxide of tungsten with ethyl alcohol yielding ethylene and water; with a third group of oxides ($Cr_2O_3,SiO_2,TiO_2,GlO,ZrO_2,UO_2,Mo_2O_5,V_2O_3.ZnO$), the two reactions first mentioned proceed simultaneously, ethylene and hydrogen appearing together. With certain higher alcohols, complications may arise; thus *iso*butyl alcohol yields a little di*iso*butylene, and benzyl alcohol gives a resinous deposit of the composition $(C_7H_6)_n$.

The reaction is greatly accelerated by a rise of temperature, in one case being fifteen times as rapid at 350° as at 260°. G. B.

Formation of Compounds in Solutions of Tartaric Acid and Sodium Molybdate. P. Quinet (*Compt. rend.*, 1908, **147**, 203—206).—The author has studied certain physical properties of solutions containing a fixed weight of *d*-tartaric acid and varying weights of sodium molybdate. The specific gravity, specific rotatory power, electrical conductivity, and freezing point of each solution have been examined and the results plotted on curves, the abscissæ of which are the weights of sodium molybdate. It is found that the curves exhibit sharply-defined maxima, which correspond in each case with a compound of one molecule of tartaric acid with two molecules of sodium molybdate. The existence of this combination was indicated by Gernez from polarimetric observations (Abstr., 1887, 540). The cryoscopic curve shows a minimum corresponding with a compound containing one molecule of each substance, but the existence of this is not confirmed by the other curves. W. O. W.

Methyl Hydrogen *d*-Tartrate. F. Tannhäuser (*Zeitsch. Kryst. Min.*, 1908, **45**, 183—184).—The crystals are rhombic

$$[a:b:c=0{\cdot}8887:1:0{\cdot}557].$$

L. J. S.

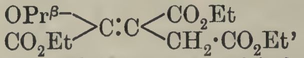
Ketonic Dibasic Acids. Edmond E. Blaise and H. Gault (*Compt. rend.*, 1908, **147**, 198—200).—This paper contains a preliminary account of a general method for the preparation of certain new α-monoketonic and $\alpha\alpha'$-diketonic dibasic acids. When ethyl oxalosuccinate is treated with hydrogen chloride in the cold and the solution boiled, hydrolysis takes place and *α-ketoglutaric acid*,

$CO_2H{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, is formed. This very reactive substance has m. p. 112—113°.

Ethyl oxalate and ethyl methylsuccinate condense in presence of sodium ethoxide to form *ethyl α′-methyl-α-oxalosuccinate*,

$$CO_2Et{\cdot}CO{\cdot}CH(CO_2Et){\cdot}CHMe{\cdot}CO_2Et,$$

which decomposes on distillation. An attempt to prepare the same substance by the action of propyl iodide on ethyl oxalosuccinate led to the formation of a derivative of the enolic form of this ester,



$$\begin{matrix}OPr^{\beta}-\\CO_2Et\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}CO_2Et\\CH_2{\cdot}CO_2Et\end{matrix},$$

b. p. 202—203°/20 mm. When treated with hydrogen bromide, this substance yields ethyl bromide, propyl bromide, and α-ketoglutaric acid.

An attempt to prepare αα′-diketoglutaric acid by the hydrolysis of ethyl dioxalosuccinate resulted in the formation of 3-*hydroxy*-2-*pyrone*-6-*carboxylic acid*, $C_6H_4O_5$. This, when heated at 200°, loses carbon dioxide and yields a substance identical with Limpricht's *iso*pyromucic acid; thus confirming the constitution ascribed to this compound by Chavanne (Abstr., 1904, i, 77). W. O. W.

Optically Active Thiolactic Acids and Thiodilactylic Acids. JOHAN M. LOVÉN (*J. pr. Chem.*, 1908, [ii], 78, 63—73).—Although two inactive thiodilactylic acids were described previously (Abstr., 1896, i, 412) as the racemic and the meso-acid respectively, attempts to resolve either into the optically active components by means of the alkaloid salts have been unsuccessful, as was also the employment of the active forms of α-phenylethylamine. Dithiodilactylic acid readily undergoes resolution into its optically active components; these on reduction yield the corresponding optically active thiolactic acids, which on treatment with α-bromopropionic acid in alkaline solution yield the optically active thiodilactylic acids.

i-Thiolactic acid (Abstr., 1884, 1298) is best prepared by reduction of trithiodilactylic acid with sodium amalgam in dilute sulphuric acid solution. On treatment with a ferric salt in acid solution, addition of an excess of potassium carbonate, and exposure to air, it yields a mixture of *r*- and *i*-dithiodilactylic acids. The r-*acid* separates in slender needles on addition of hydrochloric acid to the concentrated aqueous solution of the potassium salts. On treatment of the *r*-acid with *d*- or *l*-α-phenylethylamine in aqueous solution, the d-*base* d-*acid* salt, or the l-*base* l-*acid* salt, $S_2(CHMe{\cdot}CO_2H)_2,CHPhMe{\cdot}NH_2$, separates in long, glistening needles, the isomeric salt remaining in solution. d-*Dithiodilactylic acid* crystallises in rhombic plates, m. p. 116·5°, $[\alpha]_D$ +429°.

The optically active thiolactic acids are prepared by reduction of *d*- and *l*-dithiodilactylic acids, or their α-phenylethylamine salts, by means of sodium amalgam. l-*Thiolactic acid*, b. p. about 99—101°/15 mm., $D^{19{\cdot}2}$ 1·193, $[\alpha]_D^{15}$ −45·47°, closely resembles the *r*-acid. The *mercuric* derivative, $Hg(S{\cdot}CHMe{\cdot}CO_2H)_2$, was analysed.

The optically active *thiodilactylic acids* crystallise in large, rhombic prisms, m. p. 117°; the *l*-acid has $[\alpha]_D$ −190·0°. A solution of the two isomerides deposits the inactive acid, m. p. 125°, crystallising in monoclinic prisms, which is therefore the racemic form (*loc. cit.*). *l*-Thiodilactylic acid is formed also by the action of sodium sulphide on *d*-α-bromopropionic acid, the rotatory power being reversed by the substitution of sulphur for bromine. G. Y.

The Fission of Sugars [Sucroclasm]. I. Action of Zinc Carbonate on Formaldehyde Solutions. WALTHER LÖB (*Biochem. Zeitsch.*, 1908, **12**, 78—96).—In addition to a number of theoretical arguments, the following experiments are adduced in support of the author's view that alcoholic fermentation does not take place through the intermediate formation of lactic acid, but that it consists in a breaking-down of the sugar to H·C·OH groups, with subsequent synthesis to alcohol and carbon dioxide. By boiling 40% formaldehyde solution with two volumes of 30% potassium hydroxide, there are not only formed methyl alcohol and formic acid, as found by Nef (Abstr., 1905, i, 3), but also non-volatile hydroxy-acids (probably di- and tri-hydroxybutyric acids). By boiling 200 c.c. of 20% formaldehyde solution with 20 grams of zinc carbonate for several days, there are formed, in addition to the above products, acetol, $COMe\cdot CH_2\cdot OH$, and methylketol, $COMe\cdot HCMe\cdot OH$, which are isolated after distillation with steam as osazones. The zinc carbonate does not act as an oxidising agent, since zinc dust has the same qualitative effect. G. B.

Perseulose, a New Crystalline Sugar with Seven Carbon Atoms. GABRIEL BERTRAND (*Compt. rend.*, 1908, **147**, 201—203. Compare Abstr., 1898, i, 550).—The best bacterial culture for the oxidation of perseitol is that obtained by the spontaneous seeding of the juice of mountain ash berries. A 45% yield of *perseulose* is obtained. The new sugar has a sweet taste; the crystals resemble those of dextrose, but are better defined. The crystals are anhydrous, and have the composition $C_7H_{14}O_7$. They decompose on heating, and have no definite m. p.; on the Maquenne block they melt at about 110—115°. A freshly-prepared 10% aqueous solution has α_D^{25} not less than $-90°$; this falls rapidly, however, and after several hours becomes constant at $-81°$. The cupric reducing power of perseulose is less than that of dextrose, but considerably greater than that of sorbose.

The *osazone*, $C_{19}H_{24}O_5N_4$, crystallises from alcohol in silky needles, m. p. about 233°. W. O. W.

Products of the Reaction between Lactose and Calcium Hydroxide. HEINRICH KILIANI (*Ber.*, 1908, **41**, 2650—2658).—Some of the products of the reaction between lactose and calcium hydroxide have been examined, but the investigation of the "residue" presented considerable difficulty (this vol., i, 128). The present communication deals with this difficulty. The reaction mixture is freed from the calcium salts of *iso*saccharin and *meta*-saccharin, and the resulting mother liquor, after removal of all the calcium by oxalic acid, is evaporated to a syrup, which is divided into four parts by extraction with (I) absolute ether (five times); (II) one part of absolute alcohol and two parts of ether, dried by calcium chloride (four times); (III) a mixture of equal parts of the preceding solvents (twice), and (IV) absolute alcohol (twice). Each extraction, after removal of the solvents, is oxidised by nitric acid, D 1·4 (in the case of IV, D 1·2), whereby the most labile constituents are decomposed completely, whilst the saccharine substances are oxidised to di- and tri-basic acids, which can be more easily separated and characterised than the constituents of the original "residue." The author claims that the method must give some information as to the presence of compounds containing more or less than six atoms of carbon, and also as to the nature of the carbon chains in the products of the reaction between lactose and calcium hydroxide.

The paper contains a mass of detail unsuitable for abstraction. The main result is the detection of *l*-tartaric acid and of a tribasic *acid*, $C_6H_8O_8$ (probably identical with the α-γ-dihydroxypropane-α : α : γ-tricarboxylic acid obtained from *iso*saccharin), among the oxidation products of extracts II and III, and of a new dibasic *acid*, $C_6H_{10}O_7$, m. p. 159—160°, among the oxidation products of extract IV. Of this acid, which is feebly dextrorotatory, the *zinc*, *calcium*, *copper*, and *cadmium* salts are mentioned. C. S.

Synthesis of Glucosides: Derivatives of Xylose. Hugh Ryan and George Ebrill (*Sci. Proc. Roy. Dubl. Soc.*, 1908, **11**, 247—252. Compare Abstr., 1904, i, 223; Ryan, Trans., 1899, **75**, 1054; Ryan and Mills, Trans., 1901, **79**, 704).—A résumé is given of the work of various authors on the synthesis of acetylchloro-pentoses and -hexoses and of the corresponding glucosides. The preparation of a crystalline acetylchloroxylose and its conversion into a tetra-acetylxylose and into α-naphthyl- and carvacryl-xylosides are now described. Although the constitution of the acetylchloropentoses is uncertain, unless it is assumed that acetylchloroarabinose is the α-compound because Purdie and Rose obtained from it a product which they consider to be α-methylarabinoside (Trans., 1906, **89**, 1204), the phenol derivatives must be β-pentosides, since Fischer and Armstrong have shown that only β-hexosides are formed from both α- and β-acetylchlorohexoses in alkaline solution (Abstr., 1901, i, 671).

Acetylchloroxylose, $C_{11}H_{15}O_7Cl$, prepared by digesting xylose with acetyl chloride in a sealed tube in ice-water, separates from alcohol-chloroform in crystals, m. p. 101°, and on prolonged boiling with alcohol is converted into a non-reducing *substance*.

β-α-Naphthylxyloside, $C_{15}H_{16}O_5$, obtained by shaking acetylchloroxylose with α-naphthol and potassium hydroxide in alcoholic solution, crystallises from dilute alcohol in long needles, m. p. 192—193°, reduces Fehling's solution only after hydrolysis with dilute sulphuric acid, and is not hydrolysed by emulsin.

Carvacrylxyloside, $C_{15}H_{22}O_5$, prepared from carvacrol and acetylchloroxylose, crystallises from boiling water in long needles, m. p. 105°, and resembles β-α-naphthylxyloside in its behaviour towards Fehling's solution, but is more soluble in aqueous potassium hydroxide than in water.

When treated with silver acetate and glacial acetic acid, acetylchloroxylose is converted into tetra-acetylxylose, m. p. 119° (124°; Stone, Abstr., 1894, i, 104). G. Y.

Theoretical Investigations on the Charring of Wood. I. Dry Distillation of Cellulose. Peter Klason, Gust. von Heidenstam, and Evert Norlin (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 1, 1—34).—The authors have investigated the products obtained by the dry distillation of cellulose derived from various sources. The results show that the charring of cellulose proceeds mainly according to the equation: $8C_6H_{10}O_5 = C_{30}H_{18}O_4$ (cellulose charcoal) $+ 23H_2O + 4CO_2 + 2CO + C_{12}H_{16}O_3$ (remaining products). The velocity of this reaction begins to become considerable at about 270°. At this temperature the dry distillation of cellulose is an exothermic process, the heat of the reaction being about 6% of the heat of combustion of cellulose. The gases evolved during the distillation have a heating value of about 3·5% of the heat of combustion of the cellulose, and include hydrogen and aromatic hydrocarbons. Methyl alcohol is not formed during the dry distillation of cellulose, and must hence be derived from the lignin of the wood. Acetic acid is formed during the dry distillation of cellulose, beech and birch cellulose yielding more of this acid than cotton, or fir or pine cellulose. T. H. P.

Chemical Composition of Pine-wood. I. Peter Klason (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 5, 1—20).—From the liquid obtained by boiling pine-wood with calcium hydrogen sulphite, the author has prepared *barium lignosulphonate*, $C_{40}H_{44}O_{17}S_2Ba$, which in medium concentrations exhibits cryoscopic behaviour corresponding with a molecular weight of 4378—4675. It is assumed that lignin itself has the composition $C_{40}H_{44}O_{17}S_2Ba - BaH_2S_2O_6 = (C_{40}H_{42}H_{11})_n$. Both barium lignosulphonate and lignin give many colour reactions almost identical with those exhibited by coniferyl alcohol, and the latter, when treated with calcium hydrogen sulphite, yields a salt closely resembling calcium lignosulphonate. It is probable that lignin is formed by the condensation of coniferyl or hydroxyconiferyl alcohol. Both coniferyl alcohol and lignin are readily resinified by acids. Lignin contains 4OMe and 4OH per 40 carbon atoms, but lignosulphonic acid contains less than 4OMe. The author suggests the name "insoluble tannin" for lignin, owing to the great resemblance between the two substances; the side groups are probably in the same positions in lignin as in gallic acid. In lignosulphonic acid, part of the sulphurous acid is tightly and part loosely bound. T. H. P.

Chemical Composition of Pine-wood. II. Peter Klason and Oscar Fagerlind (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 6, 1—10).—In order to ascertain whether lignin occurs in wood combined with sugars or other carbohydrates to form glucosidic compounds, the authors have investigated the matters extracted from pine-wood by boiling water, and by the latter and alcohol used alternately.

It is found that boiling water dissolves about 12% of the dry matter of the wood, about 10% consisting of wood-gum and 2% of substances resembling true lignin. The wood-gum obtained is only sparingly soluble in alkali solution, and contains 25% of xylose, 6% of mannose, and traces of galactose, the remainder apparently consisting of unknown sugars. The other substances, resembling lignin, extracted by water consist partly of coniferyl alcohol and of a substance which is apparently a dimeric form of hydroxyconiferyl alcohol or similarly-constituted compound. Lignin does not occur in wood in combination with carbohydrates. T. H. P.

Constitution of Certain Cyanogen Compounds. F. CARLO PALAZZO and GIUSEPPE SCELSI (*Gazzetta*, 1908, **38**, i, 659—681. Compare Palazzo and Carapelle, Abstr., 1907, i, 195).—The authors have applied the action of diazomethane to thiocyanic acid, cyanamide, and cyanuric and thiocyanuric acids with the object of determining the structure of these compounds. In each case, only one of the two possible isomeric esters was obtained, the yield being quantitative.

Cyanuric acid and diazomethane yield only trimethyl *iso*cyanurate, a result which confirms Hantzsch's conclusion (Abstr., 1906, i, 146) that solid cyanuric acid is a complete pseudo-acid containing three CO·NH groups, and is, hence, tricarbimide.

On the other hand, thiocyanic acid yields methyl thiocyanate free from any trace of compound capable of combining with ammonia, so that the acid has the normal structure N:C·SH.

Thiocyanuric acid and diazomethane give a mixed trimethyl derivative, in which part of the methyl is combined with sulphur and part with nitrogen. This acid is, hence, a partial pseudo-acid, since it forms a completely normal trisodium salt, whilst in the free state a part (one-third or two-thirds) of the HCNS groups is not directly halogenic or salt-forming.

With cyanamide, diazomethane or diazoethane yields a trisubstituted *iso*melamine, which can only be formed by the polymerisation of the compound NH:C:NMe (or Et), so that cyanamide must be regarded as carbodi-imide, NH:C:NH. T. H. P.

Tautomerism of the Cyanogen Compounds. H. GUILLEMARD (*Ann. Chim. Phys.*, 1908, [viii], **14**, 311—432).—The paper commences with an historical résumé of the controversy concerning the isomerism of the nitriles and the carbylamines. This is followed by a detailed description of the analytical methods previously devised (Abstr., 1907, i, 141) for the estimation of the nitriles and the carbylamines when alone, when mixed together, and when present in the mixture resulting from the action of an alkylating agent on a metallic cyanide. A complete account of experiments on the polymerisation and isomeric change of the carbylamines, the results of which have been previously published (Abstr., 1907, i, 197), is given. When the mixture of phenylcarbylamine, aniline, and diphenylformamidine resulting from the action of alcoholic potash on a solution of aniline in chloroform is treated with silver cyanide, and the phenyl argenticyanide produced treated with potassium cyanide, after washing with ether, the product consists, not of phenylcarbylamine, but of a reddish-brown *substance*, crystallising in long, silky needles, m. p. 113°, which, when heated above its melting point, regenerates the carbylamine.

The author discusses the stereochemistry of nitrogen in the nitriles and carbylamines, and points out that the nitrogen only becomes quinquevalent after the saturation of the carbon. Thus when ethylcarbylamine dibromide is treated with hydrogen sulphide in carbon disulphide solution, ethylthiocarbimide and ethyl dibromocarbimide hydrobromide are formed: $NEt\colon CBr_2 + H_2S = NEt\colon CS + 2HBr$; $NEt\colon CBr_2 + HBr = NHEtBr\colon CBr_2$, whilst hydrogen chloride and ethyl iodide give analogous compounds. Ethyl alcohol reacts very violently with ethylcarbylamine dibromide, giving hydrogen and ethyl bromides and Gal's ethylcarbimide hydrobromide, $NHBrEt\colon CO$.

The third part of the paper is devoted to a detailed account of the experiments (Abstr., 1907, i, 300) on the action of alkylating agents (alkyl iodides and alkali alkyl sulphates) on many simple and complex metallic cyanides.

Finally, the author has determined the heats of combustion of some carbylamines and alkyl argenticyanides. The carbylamines, in order to secure complete combustion, were weighed in small glass vessels, covered with a weighed film of collodion, and, to the same end, a small quantity of water was introduced into the calorimetric bomb to avoid the deposition of carbon beneath the glass vessel. The following are the results obtained:

	Molecular heat of combustion.	Molecular heat of formation.
Methylcarbylamine	+320·1 Cal.	−28·0 Cal.
Ethylcarbylamine	480·1 ,,	−24·7 ,,
n-Propylcarbylamine	638·9 ,,	−20·2 ,,
*iso*Butylcarbylamine	795·0 ,,	−13·0 ,,
*iso*Amylcarbylamine	948·15 ,,	−2·85 ,,
Allylcarbylamine	608·8 ,,	−59·1 ,,
Benzylcarbylamine	1045·35 ,,	−49·45 ,,

By extrapolation from these figures, the values +159·1 Cal. and −31·0 Cal. are obtained for the heats of combustion and formation of the lowest member of the homologous series, namely, carbylamine itself, HNC, whilst the values +136 Cal. and −7·8 Cal. are similarly deduced for hydrogen cyanide, HCN, from the numbers observed by Berthelot for acetonitrile and propionitrile. Since the values experimentally observed by Berthelot for hydrocyanic acid are +159·3 Cal. and −30·5 Cal. respectively, the thermochemical evidence indicates that this acid is a carbylamine and not a nitrile.

Propylcarbylamine, $NPr^{a}\vdots C$, prepared by the action of propyl iodide on silver cyanide and subsequent decomposition of the propyl argenticyanide with potassium cyanide, is a liquid, b. p. 99·5°. iso*Butylcarbylamine*, prepared similarly, has b. p. 110—111°.

The alkyl argenticyanides are prepared either by melting together molecular quantities of potassium argenticyanide and the alkali alkyl sulphate, or by the addition of silver cyanide to the carbylamine dissolved in ethyl alcohol. They are well-crystallised, colourless compounds, which decompose at the ordinary temperature, evolving the carbylamine, and are decomposed by boiling aqueous alkali hydroxides, by strong acids, and by halogens, but not by hydrogen sulphide. Owing to their instability, their heats of combustion could only be determined accurately in the presence of excess of the carbylamines.

The following are the results obtained:

	Molecular heat of combustion.	Molecular heat of formation.	Heat of combination (AgNC + RNC).
Methyl argenticyanide ...	+ 440·4 Cal.	− 54·0 Cal.	+ 7·0 Cal.
Ethyl argenticyanide......	600·5 ,,	− 50·8 ,,	+ 6·9 ,,
n-Propyl argenticyanide..	759·5 ,,	− 46·5 ,,	+ 6·7 ,,
*iso*Butyl argenticyanide...	916·4 ,,	− 40·1 ,,	+ 5·9 ,,
*iso*Amyl argenticyanide...	1071·0 ,,	− 31·4 ,,	+ 4·45 ,,

These figures show that the argenticyanides as well as the carbylamines are strongly endothermic compounds, whilst the combination of silver cyanide with the carbylamine is exothermic. The gradual decrease of the values in the last column explains the increase in the tension of dissociation with increasing carbon-content.

Ethyl cuprocyanide, large, colourless prisms, *propyl cuprocyanide*, rhombic tablets, and iso*butyl cuprocyanide*, rhombic prisms of the general formula CuN:C:C:NR, have similar properties to the silver compounds, and are prepared in a similar manner.

The conclusions drawn are that hydrocyanic acid and its metallic salts must be formulated as *iso*cyanides, giving carbylamines with alkylating agents, that the organometallic compounds of the carbylamines decompose into nitriles and carbylamines, the proportion of each depending on the temperature and nature of the alkyl group present, and that the cyanides do not exhibit any phenomena of tautomerism. E. H.

Preparation of Halogen-substituted Acetonitriles. Wilhelm Steinkopf (*Ber.*, 1908, 41, 2540—2542. Compare Braun, this vol., i, 627, 675).—Chloroacetonitrile is readily prepared in a 70% yield by distillation of a mixture of chloroacetamide and phosphoric oxide from a glass flask (compare Scholl, Abstr., 1897, i, 9) under 200 mm. and, finally, under 11 mm. pressure (Abstr., 1907, i, 490). Bromoacetonitrile is obtained in the same manner from bromoacetamide in a 60% yield (Abstr., 1905, i, 756). Trichloro- and tribromo-acetonitriles are best prepared by distillation of the amides with phosphoric oxide under the ordinary pressure. Iodoacetonitrile is obtained in good yields by the action of potassium iodide on crude chloroacetonitrile. G. Y.

Double Sulphate of Guanidine and Aluminium. F. Ferraboschi (*Proc. Camb. Phil. Soc.*, 1908, 14, 471—474).—From a solution containing approximately equivalent quantities of guanidine and aluminium sulphates, a double salt of the composition

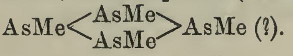
$$(CN_3H_5)_2H_2SO_4,Al_2(SO_4)_3,12H_2O$$

crystallises in large, well-developed, hexagonal prisms terminated by basal planes. The crystals exhibit a perfect basal cleavage, and probably belong to the scalenohedral class of the rhombohedral system; $D^{13\cdot5}$ 1·806. H. M. D.

Reactions of the Arsines. William M. Dehn (*Amer. Chem. J.*, 1908, 40, 88—127. Compare Abstr., 1905, i, 184; 1906, i, 150, 341).—The reactions of arsenic compounds cannot always be explained on the basis either of ionic or of kineto-molecular mechanics. Most of the arsenic reactions are non-electrolytic, and between the initial compounds and the most easily separable end-product other compounds, usually crystalline, are formed and can often be separated. The present paper describes a systematic study of the reactions of the arsines, evidence being obtained showing that intermediate products are often formed and that arsenic compounds react largely by initial coalescence with the reagent. In most of the reducing actions effected by the arsines, there is evidence of an initial amalgamation of the oxidising agent and the arsine. Also, in the interaction of sodium arsenite with alkyl iodides, according to the equation $Na_3AsO_3 + RI = Na_2RAsO_3 + NaI$, the additive compound $AsIR(ONa)_3$ is formed as an intermediate product.

In the electrolytic reduction of cacodyl chloride to dimethylarsine, cacodyl is first formed, the successive reactions being $2AsMe_2Cl + 2H = AsMe_2{\cdot}AsMe_2 + 2HCl$ and $AsMe_2{\cdot}AsMe_2 + 2H = 2AsHMe_2$.

[With Elrick Williams.]—A large number of reactions of methylarsine were studied, and equations are given for the changes taking place. The reactions represented by the equations: $AsMeH_2 + HI \rightleftharpoons AsMeH_3I \longrightarrow AsMeHI + H_2$ and $AsMeHI + HI \rightleftharpoons AsMeH_2I_2 \longrightarrow AsMeI_2 + H_2$ are slow or readily reversible. Methylarsine gives (1) with propyl iodide, AsH_2MePrI, the reaction being reversible; (2) with silver nitrate, a mixture of silver methylarsinate and silver; (3) with methylarsine oxide, the compound $(AsMe)_4$ or



$$\mathrm{AsMe}<\begin{matrix}\mathrm{AsMe}\\ \mathrm{AsMe}\end{matrix}>\mathrm{AsMe}\ (?).$$

Ethylarsine reacts with (1) iodine, $AsH_2Et + I_2 = AsI_2Et + H_2$; (2) bromine, $AsH_2Et + Br_2 = AsBr_2Et + H_2$, intermediate products being formed; (3) sulphur, $AsH_2Et + S_2 = AsEtS + H_2S$; (4) mercuric chloride, $AsH_2Et + 2HgCl_2 = AsCl_2Et + 2Hg + 2HCl$; (5) mercuric iodide, $AsH_2Et + 2HgI_2 = AsI_2Et + 2HgI + H_2$; (6) stannic chloride, $AsH_2Et + 2SnCl_4 = AsCl_2Et + 2SnCl_2 + 2HCl$; (7) arsenic trichloride, $8AsH_2Et + 8AsCl_3 = (AsEt)_4 + 4AsCl_2Et + 16HCl + 8As$; (8) propyl iodide, giving *ethyltripropylarsonium iodide*, $AsEtPr_3I$, m. p. 237° (decomp.); (9) *iso*propyl iodide, giving ethyltri*iso*propylarsonium iodide, which decomposes at its melting point according to the equations: $AsEtPr^{\beta}_3I = AsPr^{\beta}_3 + EtI$ and $2AsEtPr^{\beta}_3I = AsPr^{\beta}_3I_2 + C_4H_{10} + AsPr^{\beta}_3$.

Benzylarsine, $AsH_2{\cdot}CH_2Ph$, prepared by reducing benzylarsinic acid by means of amalgamated zinc dust and hydrochloric acid, is a faintly yellow liquid, b. p. 140°/262 mm., oxidises in the air to benzylarsinic acid, and forms a *platinichloride*, $C_7H_7AsH_2,PtCl_4$.

Tripropylarsine, $AsPr^{\alpha}_3$, prepared by the interaction of propyl chloride, arsenic trichloride, and sodium, has b. p. 167°/90 mm. and 158°/73 mm.

The decomposition of various arsenic derivatives by heat has been studied, the reactions being as follows: *iso*amylarsinic acid,

$$2AsO_3H_2{\cdot}C_5H_{11} = 2C_5H_{11}{\cdot}OH + As_2O_3 + H_2O;$$

phenylarsinic acid, $2AsO_3H_2Ph = Ph_2O + As_2O_3 + 2H_2O$; phenylarsine, $3AsH_2Ph = Ph_3As + 2As + 3H_2$; methylarsine, $2AsH_2Me = 2CH_4 + 2As + H_2$; ethylarsine, $2AsH_2Et = 2C_2H_6 + 2As + H_2$ and $3AsH_2Et = Et_3As + 2As + 3H_2$; di*iso*amylarsine, $6AsH(C_5H_{11})_2 = 4As(C_5H_{11})_3 + 2As + 3H_2$ and $2AsH(C_5H_{11})_2 = C_5H_{10} + C_5H_{12} +$

$C_{10}H_{22} + 2As$; diphenylarsine, $6AsHPh_2 = 4AsPh_3 + 2As + 3H_2$ and $2AsPh_3 = 3C_{12}H_{10} + 2As$; tripropylarsine, $4AsPr^{\alpha}_3 = (AsPr^{\alpha})_4 + 4C_6H_{14}$; triethylarsine, $4AsEt_3 = (AsEt)_4 + 4C_4H_{10}$; benzylarsine,

$$4AsH_2\cdot CH_2Ph \longrightarrow (As\cdot CH_2Ph)_4 + 4H_2;$$

cacodyl, $4AsMe_2\cdot AsMe_2 \longrightarrow 4AsMe_3 + (AsMe)_4$.

[With BURTON B. WILLCOX.]—Dimethylarsine gives the following reactions: (1) With phenylarsine dichloride it yields dimethylarsinephenylarsine dichloride, $AsCl_2Ph\cdot AsHMe_2$, which decomposes rapidly in the air; (2) with di*iso*amylarsine chloride, dimethyldi*iso*amylcacodyl, $AsMe_2\cdot As(C_5H_{11})_2$, is obtained; (3) with propyl iodide it yields *dimethylpropylarsonium iodide*, $AsHMe_2Pr^{\alpha}I$, which, with *iso*amyl iodide, gives *dimethylpropyl*iso*amylarsonium iodide*,

$$AsMe_2Pr(C_5H_{11})I;$$

(4) with acetyl iodide it forms $AsHMe_2AcI$ which decomposes, giving $AsMe_2I + CH_3\cdot CHO$; (5) with ethyl chlorocarbonate, dimethylarsine reacts thus: $AsHMe_2 + Cl\cdot CO_2Et \longrightarrow AsMe_2Cl + H\cdot CO_2Et$; (6) with sulphur dichloride, $2AsHMe_2 + SCl_2 \longrightarrow 2AsMe_2Cl + S$; (7) with arsenic trioxide, $2AsHMe_2 + As_2O_3 = (AsMe)_4 + H_2O + O_2$; (8) with arsenic trichloride, $4AsHMe_2 + 2AsCl_3 = (AsMe)_4 + 2AsMe_2Cl + 4HCl$.

Di*iso*amylarsine and propyl iodide yield dipropyldi*iso*amylarsonium iodide, $AsPr^{\alpha}_2(C_5H_{11})_2I$, and cacodyl and propyl iodide, *dimethyldipropylarsonium iodide*, $AsMe_2Pr_2I$, which, with mercuric chloride, gives a white *precipitate*, $AsMe_2Pr_2I,HgCl_2$. T. H. P.

***cyclo*Hexadienes. II.** NICOLAI D. ZELINSKY and A. GORSKY (*Ber.*, 1908, **41**, 2630—2634. Compare this vol., i, 619).—A pronounced exaltation of the molecular refraction is not shown by the following hydrocarbons containing conjugate double linkings. 1-Methyl-Δ^1-*cyclo*hexene yields a *dibromide*, b. p. 100—102°/12 mm., from which by means of quinoline, 1-*methyl*-$\Delta^{2:6}$-cyclo*hexadiene* is obtained, which has b. p. 110°(corr.)/741 mm., D^{20}_4 0·8292, n^{20}_D 1·4710, and gives a blood-red coloration with alcoholic sulphuric acid and a bluish-violet with nitric acid (D 1·40). 1 : 3-Dimethyl*cyclo*hexene yields a *dibromide*, b. p. 130—135°/35 mm., which by distillation with quinoline yields 1 : 3-*dimethyl*-$\Delta^{2:4}$-cyclo*hexadiene*, b. p. 129—130°/745 mm., D^{20}_4 0·8225, n^{20}_D 1·4675, $[\alpha]_D$ 27·38°. 1 : 4-Dimethyl*cyclo*hexan-4-ol and aqueous oxalic acid yield 1 : 4-*dimethyl*-Δ^3-cyclo*hexene*, b. p. 128·5° (corr.), D^{20}_4 0·8005, n^{20}_D 1·4457, the *dibromide* of which, by repeated distillation with quinoline, yields 1 : 4-*dimethyl*-$\Delta^{2:4}$-cyclo*hexadiene*, b. p. 132·5—133·5°(corr.)/740 mm., D^{20}_4 0·8223, n^{20}_D 1·4675. 1 : 2-Dimethyl*cyclo*hexan-2-ol and aqueous oxalic acid yield 1 : 2-*dimethyl*-cyclo*hexene*, b. p. 135·5—136·5° (corr.), D^{20}_4 0·8226, $n^{21·5}_D$ 1·4580, the derivatives of which will be considered later. C. S.

Mechanism of the Autoracemisation of Optically Active Ammonium Salts and the State of Quaternary Ammonium Salts in Solution. EDGAR WEDEKIND and F. PASCHKE (*Ber.*, 1908, **41**, 2659—2665).—von Halban's measurements with inactive ammonium salts (Abstr., 1907, ii, 246) do not decide whether the racemisation of the active salts is due solely to decomposition into a tertiary base and an alkyl haloid, or is conditioned partly by intramolecular changes. That the latter alternative may be of influence is shown by the fact that active methylallyltetrahydroquinolinium iodide in methyl alcohol racemises with extraordinary velocity, although theoretically it should be stable in this solvent. The authors have therefore examined phenylbenzylmethylallyl-(or propyl)ammonium bromide and iodide polarimetrically, cryoscopically, by a slightly modified form of von Halban's titrimetric method, and by direct weighing of the undecomposed salt precipitated by ether. In every case the velocity constant of the decomposition agrees well with that of the racemisation. Ammonium salts, therefore, in suitable solvents (see later) decompose into a tertiary base and an alkyl haloid, a phenomenon which in the case of active salts is accompanied by an equally rapid diminution of the rotation. The deduction that active and inactive salts of the same base must decompose at the same rate has been verified. Moreover, the point of equilibrium of the system $RR'R''R'''NX \rightleftarrows R'R''R'''N + RX$ must be the same for the active and the inactive modification of the same salt (compare von Halban, *loc. cit.*). This point differs greatly in bromides and iodides; in the former it corresponds with 40—50% of unchanged salt, and in the latter to 6%, at 25°. The preceding equation does not represent truly the condition of affairs in the solution, since the partition-coefficient in chloroform and cryoscopic measurements in bromoform indicate that ammonium salts are present in the solution in the bimolecular state.

The nature of the solvent is of importance. Water and alcohol at 45° do not decompose quaternary ammonium salts appreciably, but in solvents with a small dielectric constant, such as tetrachloroethane, benzene, carbon disulphide, or ethylene tetrabromide (with the addition of alcohol to facilitate solution), the decomposition of an active ammonium salt can be followed with the polarimeter.

C. S.

Isomerism of Carbethoxydiglycylglycine Ester and the Stability of *N*-Carboxylic Acids. HERMANN LEUCHS and FREDERICK B. LA FORGE (*Ber.*, 1908, **41**, 2586—2596. Compare Leuchs and Manasse, Abstr., 1907, i, 770).—Carbethoxy-*N*-phenylglycylglycylglycine ester exists in two isomeric forms. The α-compound,

$$CO_2Et\cdot NPh\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

is obtained synthetically by the action of glycylglycine ester on carbethoxy-*N*-phenylglycyl chloride. When suitably hydrolysed, it yields the β-*N*-phenylglycylglycine-*N*-carboxylic acid,

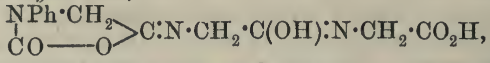
$$CO_2H\cdot NPh\cdot CH_2\cdot C(OH)\colon N\cdot CH_2\cdot C(OH)\colon N\cdot CH_2\cdot CO_2H,$$

the silver salt of which reacts with ethyl iodide, yielding the isomeric β-ester.

*α-Carbethoxy-*N*-phenylglycylglycylglycine ester* crystallises from benzene in small, colourless needles, m. p. 135—136°. When hydrolysed with sodium hydroxide (1 mol.), it yields *α-carbethoxy-*N*-phenylglycylglycylglycine*,

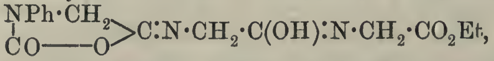
$$CO_2Et\cdot NPh\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

which can also be synthesised from glycylglycine and carbethoxyphenylglycyl chloride. It crystallises from ethyl acetate in needles, m. p. 145—146° after sintering at 141°, or from water in hydrated needles. When boiled with sodium hydroxide (2 mols.) and then acidified, the acid ester yields the *lactone* of *β-phenylglycylglycylglycine*-N-*carboxylic acid*,



$$\begin{array}{l}\mathrm{NPh{\cdot}CH_2} \\ \mathrm{CO{-}{-}{-}O}\end{array}\!\!>\mathrm{C{:}N{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}CH_2{\cdot}CO_2H},$$

which crystallises from water and has m. p. 212—213° (corr.). Alcoholic hydrochloric acid converts this lactone into the *β-lactone ester*,



$$\begin{array}{l}\mathrm{NPh{\cdot}CH_2} \\ \mathrm{CO{-}{-}{-}O}\end{array}\!\!>\mathrm{C{:}N{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}CH_2{\cdot}CO_2Et},$$

m. p. 182—183° (corr.). *β*-N-*Phenylglycylglycylglycine*-N-*carboxylic acid*,

$$\mathrm{CO_2H{\cdot}NPh{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}CH_2{\cdot}CO_2H},$$

is obtained by carefully hydrolysing the *α*-ester, and when boiled with water or dilute hydrochloric acid readily yields the lactone acid, m. p. 212—213°. The *β*-ester, obtained from the silver salt of the *β*-acid, is a thick oil, and when boiled with alcoholic hydrochloric acid yields the lactone ester, m. p. 182—183°.

Carbethoxyglycyl-N-*phenylglycine*, $C_{13}H_{16}O_5N_2$, obtained by hydrolysing the corresponding ester (Abstr., 1907, i, 770), crystallises from benzene in colourless plates, m. p. 133—134°. The corresponding chloride reacts with ethyl glycine, yielding *ethyl carbethoxyglycyl*-N-*phenylglycylglycine*, $\mathrm{CO_2Et{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NPh{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et}$, which crystallises from benzene or hot water in large prisms, m. p. 144—145° (corr.). When the ester is boiled with three equivalents of barium hydroxide, only some 30% of the theoretical amount of carbon dioxide is removed. The elimination of carbon dioxide is probably due to the fact that part of the ester is not transformed into the *β*-isomeride, but is directly hydrolysed, and the resulting *α*-acid immediately loses carbon dioxide.

Ethyl carbethoxyglycyl-N-*phenylglycyl*-N-*phenylglycine*,

$$\mathrm{CO_2Et{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NPh{\cdot}CH_2{\cdot}CO{\cdot}NPh{\cdot}CH_2{\cdot}CO_2Et},$$

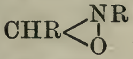
obtained by condensing ethyl phenylglycine with carbethoxyglycyl-*N*-phenylglycyl chloride, has not been obtained in a crystalline form; the corresponding *acid*, $C_{21}H_{23}O_6N_3$, crystallises from ethyl acetate in nodules and contains $1H_2O$. When rapidly heated, it melts and decomposes at 128—130°. When boiled with excess of sodium hydroxide, the elimination of carbon dioxide is almost theoretical.

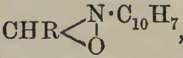
Ethyl carbethoxyglycylsarcosine,

$$\mathrm{CO_2Et{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}CO_2Et},$$

crystallises from ether in long prisms, m. p. 54—55°, and, when hydrolysed with sodium hydroxide, loses an appreciable amount of carbon dioxide.

The results support the view that it is the *α*-(lactam)compounds which yield carbon dioxide, and when substituents are attached to the nitrogen atom so that molecular rearrangement into the isomeric *β*-(lactim)compound cannot take place, carbon dioxide is always eliminated during hydrolysis. J. J. S.

***N*-α-Naphthylhydroxylamine. II.** JOHANNES SCHEIBER [and, in part, ERNST BECKMANN] (*J. pr. Chem.*, 1908, [ii], 78, 74—80. Compare Abstr., 1904, i, 867).—Two of the most characteristic reactions of the β-substituted hydroxylamines are the formation of *N*-aldoxime ethers,  $CHR<\overset{NR}{\underset{O}{|}}$, by condensation with aldehydes, and of disubstituted hydroxycarbamides, $OH·NR·CO·NHPh$, by addition of phenylcarbimide (Beckmann, Abstr., 1898, i, 22). Although containing the elements of a mol. of water more than other *N*-arylhydroxylamines, *N*-α-naphthylhydroxylamine is found also to undergo these typical reactions.

The following N-α-*naphthylaldoximes*,  $CHR<\overset{N·C_{10}H_7}{\underset{O}{|}}$, are described:

R = Ph: yellow crystals, m. p. 106·5°, decomposes, becoming red on exposure to light. $R = C_6H_4·OMe(p)$: yellow crystals, m. p. 159°. $R = C_6H_4·OH(o)$: yellow crystals, m. p. 153°. $R = C_6H_4·NO_2(m)$: m. p. 147°.

a-*Hydroxy*-b-*phenyl*-a-α-*naphthylcarbamide*, $OH·N(C_{10}H_7)·CO·NHPh$, formed from *N*-α-naphthylhydroxylamine and phenylcarbimide, is obtained in white crystals, m. p. 126°, and gives an intense blue coloration with ferric chloride in alcoholic solution.

a-*Hydroxy*-b-p-*tolyl*-a-α-*naphthylcarbamide*,

$$OH·N(C_{10}H_7)·CO·NH·C_7H_7,$$

formed from N-α-naphthylhydroxylamine and *p*-tolylcarbimide, separates from alcohol in crystals, m. p. 147°, and gives a blue coloration with ferric chloride.

a-*Hydroxy*-b-*phenyl*-a-α-*naphthylthiocarbamide*,

$$OH·N(C_{10}H_7)·CS·NHPh,$$

prepared from *N*-α-naphthylhydroxylamine and phenylthiocarbimide, forms nodular crystals, m. p. 119°, and gives a black solution with alcoholic ferric chloride. G. Y.

***N*-α-Naphthylhydroxylamines. III.** JOHANNES SCHEIBER and PAUL BRANDT (*J. pr. Chem.*, 1908, [ii], 78, 80—92. Compare preceding abstract).—The *N*-aldoxime ethers derived from *N*-α-naphthylhydroxylamine behave towards mineral acids and alkalis in the same manner as other *N*-arylaldoximes, yielding the aldehyde and transformation products of the *N*-α-naphthylhydroxylamine, chiefly azoxynaphthalene. On the other hand, the isolation of an additive compound of *N*-α-naphthylhydroxylamine and phenylcarbimide has not been achieved. *N*-Aldoxime ethers, in general, are transformed by acid chlorides or anhydrides into the isomeric amides. The transformation takes place readily and at low temperatures with benzoyl or acetyl chloride, benzoylated and acetylated amides being formed with an excess of the acid chloride at high temperatures, but only at high temperatures with benzoic anhydride, when the benzoylated amide is formed. As, however, Wortmann (*Diss.*, Leipzig, 1903) found that the action of benzoic anhydride on *N*-α-naphthylbenzaldoxime leads to the formation of *N*-benzoyl-1-amino-β-naphthol, it was of interest to study the mechanism of this reaction.

It is found now that *N*-benzoyl-1-amino-*β*-naphthol is formed by the action of benzoic anhydride, not only on *N*-*α*-naphthylbenzaldoxime, but also on *N*-*α*-naphthylanisaldoxime or on *N*-*α*-naphthylhydroxylamine, in the last case being accompanied by small amounts of dibenzoyl-1-amino-*β*-naphthol, which is formed also by the action of an excess of benzoic anhydride on *N*-*α*-naphthylanisaldoxime. On the other hand, the action of benzoic anhydride on *N*-anisoyl-1-amino-*β*-naphthol leads to the formation of *O*-benzoyl-*N*-anisoyl-1-amino-*β*-naphthol, together with small amounts of *N*-benzoyl- and unchanged *N*-anisoyl-1-amino-*β*-naphthol. It is argued that the action of benzoic anhydride on *N*-*α*-naphthylaldoximes must, therefore, consist in the first place of a fission of the aldoxime with formation of *N*-*α*-naphthylhydroxylamine, and not of an addition of the anhydride to the *N*-aldoxime ether.

When gently heated with acetic anhydride, *N*-*α*-naphthylanisaldoxime yields *N*-acetyl-1-amino-*β*-naphthol (Michel and Grandmougin, Abstr., 1893, i, 171).

[For the benzoyl and anisoyl derivatives of 1-amino-*β*-naphthol, see abstract below.] G. Y.

Transformation of Benzhydroxamic Acid into Anilides. Giacomo Ponzio and R. Giovetti (*Gazzetta*, 1908, **38**, i, 655—657).—When benzhydroxamic acid is treated in alkaline solution with an aryl diazochloride, it is converted into its corresponding unstable diazo-salt, and this, when heated with alcohol, is converted into an anilide of benzhydroxamic acid.

Thus, with diazobenzene chloride, benzanilide is obtained; with *o*-diazotoluene chloride, benzo-*o*-toluidide; with *p*-diazotoluene chloride, benzo-*p*-toluidide; with *p*-diazoanisole chloride, benzo-*p*-anisidide, and with *as*-m-diazoxylene chloride, benzo-*m*-xylidide. T. H. P.

***syn*.- and *anti*-Stereoisomerism of Nitrogen Compounds.** Julius Stieglitz (*Amer. Chem. J.*, 1908, **40**, 36—46).—The author gives a résumé of the various pairs of stereoisomeric chloroimino-esters prepared by him in conjunction with Earle (Abstr., 1904, i, 39) and others, and discusses them in relation to Hantzsch and Werner's hypothesis of *syn*.- and *anti*-stereoisomerism. T. H. P.

Derivatives of 1-Amino-*β*-naphthol. Johannes Scheiber and Paul Brandt (*J. pr. Chem.*, 1908, [ii], **78**, 92—95. Compare this vol., i, 725).—*N*-Benzoyl-1-amino-*β*-naphthol, m. p. 248° (245°: Böttcher, Abstr., 1883, 1113), is prepared by heating 1-amino-*β*-naphthol hydrochloride and sodium acetate with benzoic anhydride in glacial acetic acid solution.

Dianisoyl-1-amino-β-naphthol, $C_{26}H_{21}O_5N$, formed by shaking 1-amino-*β*-naphthol with anisoyl chloride and aqueous sodium hydroxide, separates from methyl alcohol in crystals, m. p. 215°, and, when treated successively with alcoholic sodium ethoxide and hydrochloric acid, yields N-*anisoyl-1-amino-β-naphthol*, $C_{18}H_{15}O_3N$, crystallising in golden leaflets, m. p. 241—243°.

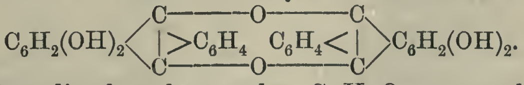
N-*Benzoyl*-O-*anisoyl*-1-*amino*-*β*-*naphthol*, $C_{25}H_{19}O_4N$, m. p. 181°, is obtained by the action of anisoyl chloride and sodium hydroxide on *N*-benzoyl-1-amino-*β*-naphthol, and yields *N*-benzoyl-1-amino-*β*-naphthol when treated with alcoholic sodium hydroxide.

O-*Benzoyl*-N-*anisoyl*-1-*amino*-*β*-*naphthol*, m. p. 189°, is formed by benzoylation of *N*-anisoyl-1-amino-*β*-naphthol, and yields this when hydrolysed with alcoholic sodium hydroxide. G. Y.

Oxidation of Eugenol by the Oxidising Ferment of Mushrooms. Formation of Dehydrodieugenol. H. Cousin and Henri Hérissey (*Compt. rend.*, 1908, **146**, 1413—1415. Compare this vol., i, 84).—Oxidation with ferric chloride or with air in presence of the oxydase from *Russula delica*, forms in very dilute eugenol solutions a precipitate of *dehydrodieugenol*, $C_{20}H_{22}O_4$, leaflets, m. p. 105—106°, giving a blue coloration with ferric chloride, and still having a double linking. *Diacetyldehydrodieugenol*, $C_{24}H_{26}O_6$, melts at 91—92°, and *dibenzoyldehydrodieugenol*, $C_{34}H_{30}O_6$, melts at 170—171°. G. B.

cycloHexanylethyl Alcohol and cycloPentanylcarbinol. Nicolai D. Zelinsky (*Ber.*, 1908, **41**, 2628—2629).—The reaction between magnesium *cyclo*hexanyl iodide and trioxymethylene in dry ether leads to the formation of cyclo*hexanylethyl alcohol*, $C_6H_{11}\cdot CH_2\cdot CH_2\cdot OH$, b. p. 206—207°/745 mm. and 97—100°/12 mm., D_4^{20} 0·9153, n_D^{20} 1·4647. cyclo*Pentanylcarbinol*, $C_5H_9\cdot CH_2\cdot OH$, obtained from magnesium *cyclo*pentanyl chloride and trioxymethylene, has b. p. 162·5—163·5° (corr.), D_4^{20} 0·9260, n_D^{20} 1·4555, forms a *phenylcarbamate*, m. p. 110° (corr.), and is oxidised to the corresponding *aldehyde* by 10% chromic acid in dilute acetic acid. C. S.

New Synthesis of Derivatives of Anthracene. Hans von Liebig (*J. pr. Chem.*, 1908, [ii], **78**, 95—96).—When fused with mandelic acid at 200—300°, the three dihydroxybenzenes form the corresponding dihydroxydiphenylmethanecarboxylic acids, but catechol and quinol yield also crystalline dyes, which in their behaviour resemble the dihydroxyanthraquinones, but are meso-ethers and are insoluble in aqueous sodium carbonate. These dyes are considered to have the constitution



$$C_6H_2(OH)_2\left\langle\begin{array}{c}C\text{———}O\text{———}C\\ |>C_6H_4\quad C_6H_4<|\\ C\text{———}O\text{———}C\end{array}\right\rangle C_6H_2(OH)_2.$$

2 : 2′ : 3 : 3′-*Tetrahydroxydianthranol meso-ether*, $C_{28}H_{16}O_5$, prepared from catechol and mandelic acid, crystallises in glistening, bronze-coloured leaflets, m. p. 264°, and dissolves in benzene or alcohol to a red, or in aqueous alkalis to a blue, solution.

1 : 1′ : 4 : 4′-*Tetrahydroxydianthranol meso-ether*, formed from quinol and mandelic acid, crystallises in violet-red needles, m. p. 298°, and dissolves in benzene or alcohol to a red, or in aqueous alkalis to a violet, solution.

2 : 5-Dihydroxydiphenylmethanecarboxylic acid lactone, m. p. 157° (153—154°: Bistrzycki and Flatau, Abstr., 1895, i, 419), obtained

from quinol and mandelic acid, 2 : 4-dihydroxydiphenylmethanecarboxylic acid lactone, m. p. 183°, from resorcinol and mandelic acid, and 2-hydroxy-4-methyldiphenylmethanecarboxylic acid lactone, m. p. 124°, from *m*-cresol and mandelic acid, give colorations with concentrated sulphuric acid. G. Y.

Cholesterol. XI. ADOLF WINDAUS (*Ber.*, 1908, 41, 2558—2568). —When the tribasic acid, $C_{25}H_{40}O_6$ (this vol., i, 265), is heated for eight hours at 75° with a mixture of equal volumes of fuming nitric and glacial acetic acids, the products are a trinitro-acid, $C_{25}H_{37}O_{12}N_3$, a tetrabasic acid, $C_{21}H_{30}O_8$, and α-hydroxy*iso*butyric acid ; the formation of the two latter may be represented by means of the equation

$$C_{25}H_{40}O_6 + 6O \longrightarrow C_4H_8O_3 + C_{21}H_{30}O_8 + H_2O.$$

The *trinitro*-acid is precipitated on the addition of water, and may be purified by washing with ethyl acetate and subsequent recrystallisation from glacial acetic acid. It forms colourless, glistening, rhombic plates, m. p. 234—235° (decomp.). It is a tribasic acid, and yields a *monorubidium* salt, $C_{25}H_{36}O_{12}N_3Rb$, which crystallises readily from 50% alcohol, and also an *acid potassium* salt, $C_{25}H_{34}O_{12}N_3K_3, C_{25}H_{37}O_{12}N_3$. When reduced with zinc dust and acetic acid, the trinitro-acid yields acetone and a nitrile, $C_{22}H_{31}O_6N$. The formation of acetone is in harmony with the view that the nitro-acid contains the grouping $NO_2\cdot CMe_2\cdot C(NO_2)_2$, and hence the original tribasic acid may be represented by the formula $CHMe_2\cdot CH_2\cdot C_{18}H_{28}(CO_2H)_3$. Among the products of reduction is a *ketonic acid*, probably

$$CHMe_2\cdot CO\cdot C_{18}H_{28}(CO_2H)_3,$$

which yields a crystalline *oxime*, $C_{25}H_{39}O_7N$, m. p. 230—231° (decomp.). The *nitrile*, $C_{22}H_{31}O_6N$, crystallises from dilute acetic acid in needles and prisms, m. p. 137—138° after sintering at 127°. It is a tribasic acid, and, when boiled with potassium hydroxide solution, yields a *tetrabasic acid*, $C_{22}H_{32}O_8$, which crystallises from dilute acetic acid in prisms, m. p. 189°. The *caesium trihydrogen* salt, $C_{22}H_{31}O_8Cs$, crystallises from alcohol in long needles.

The *tetrabasic acid*, $C_{21}H_{30}O_8 = C_{17}H_{26}(CO_2H)_4$, crystallises from hot water in anhydrous, compact prisms or quadratic plates, m. p. 234° (decomp.), or from cold solution in hydrated needles. The needles when dehydrated in a vacuum over sulphuric acid sinter to a transparent mass at about 135°, and this, when further heated, sets to a mass of quadratic plates, m. p. 234° (decomp.). It yields a *monocaesium* salt, $C_{21}H_{29}O_8Cs$, and is stable towards sodium hydroxide, nitric, sulphuric, and chromic acids, and bromine. The tetrabasic acid is also obtained when the ketonic acid, $CHMe_2\cdot CO\cdot C_{18}H_{28}(CO_2H)_3$, is oxidised with an acetic acid solution of nitric acid. J. J. S.

Cholesterol. VII. OTTO DIELS (*Ber.*, 1908, 41, 2596—2600. Compare Dorée and Gardner, Proc., 1908, 24, 173).—The crude ozonide of cholesterol contains more oxygen than as stated by Dorée and Gardner. After purification by digestion with cold alcohol, it has the composition $C_{27}H_{46}O_5$, and may be crystallised from hot acetone. It is stable and does not explode when heated. The purified ozonide is somewhat more stable towards water than the crude, but when heated in sealed tubes at 140—150° it yields a yellow resin and an aqueous solution with a pleasant odour. The close relationship between cholesterol and cholestenone has been already established by Diels and Linn (this vol., i, 164) and Willstätter and Mayer (this vol., i, 636).

J. J. S.

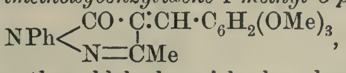
***cyclo*Pentanecarboxylic Acid and Chloro*cyclo*pentane.** Nicolai D. Zelinsky (*Ber.*, 1908, **41**, 2627—2628).—*Chloro*cyclo*pentane*, C_5H_9Cl, obtained from *cyclo*pentanol and concentrated hydrochloric acid at 110°, has b. p. 114·5—115° (corr.), D^{20}_{4} 1·0051, n^{20}_{D} 1·4510, and reacts in ethereal solution with magnesium and carbon dioxide to form *cyclo*pentanecarboxylic acid, b. p. 215·5—216° (corr.) and 104°/11 mm., D^{20}_{4} 1·0510, n^{18}_{D} 1·4534, the *amide* of which has m. p. 179° (corr.).

C. S.

Trimethylgallaldehyde [3 : 4 : 5-Trimethoxybenzaldehyde]. Synthesis of Methylsinapic Acid. Ferdinand Mauthner (*Ber.*, 1908, **41**, 2530—2533. Compare this vol., i, 348).—When heated with aqueous hydrazine hydrate in a sealed tube at 100°, 3 : 4 : 5-trimethoxybenzaldehyde forms the *azine*, $N_2[CH\cdot C_6H_2(OMe)_3]_2$, which crystallises in yellow needles, m. p. 195—196°, and gives a red coloration with concentrated sulphuric acid. The oxime of 3 : 4 : 5-trimethoxybenzaldehyde has m. p. 83—84° (Semmler, this vol., i, 558). The *benzidine* derivative, $[C_6H_4\cdot N{:}CH\cdot C_6H_2(OMe)_3]_2$, crystallises in yellow needles, m. p. 210—211°.

Methylsinapic acid (Gadamer, Abstr., 1898, i, 38) is formed by heating 3 : 4 : 5-trimethoxybenzaldehyde with acetic anhydride and sodium acetate at 140—150°. 3 : 4 : 5-*Trimethoxy-α-methylcinnamic acid*, $C_6H_2(OMe)_3\cdot CH{:}CMe\cdot CO_2H$, formed together with a neutral oil (trimethoxypropenylbenzene) from 3 : 4 : 5-trimethoxybenzaldehyde, propionic anhydride, and sodium propionate at 140—150°, crystallises in long needles, m. p. 157—158°.

4-*Phenyl*-3 : 4 : 5-*trimethoxybenzylidene*-1-*methyl*-3-*pyrazolone*,



$$\mathrm{NPh}\Big<\begin{matrix}\mathrm{CO\cdot \overset{}{C}{:}CH\cdot C_6H_2(OMe)_3}\\ \mathrm{N{=}CMe}\end{matrix},$$

obtained by heating the aldehyde with phenylmethylpyrazolone in acetic acid solution, crystallises in red needles, m. p. 141—142°.

Trimethoxybenzylidenebisacetophenone, $C_6H_2(OMe)_3\cdot CH(CH_2\cdot COPh)_2$, m. p. 105—106°. *α-Trimethoxyphenyl-β-naphthacinchonic acid*, formed by condensation of trimethylgallaldehyde with pyruvic acid and β-naphthylamine, is obtained in yellow crystals, m. p. 262—263.

G. Y.

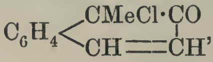
3-Chloro-6-chloroacetyltoluene [5-Chloro-*o*-tolyl Chloromethyl Ketone] and Two Chlorodinitrotoluic Acids. Franz Kunckell (*Ber.*, 1908, **41**, 2648—2650).—The reaction between aluminium chloride, *m*-chlorotoluene, and chloroacetyl chloride in carbon disulphide results in the formation of 5-*chlorotolyl chloromethyl ketone*,

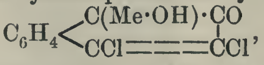
$$CH_2Cl\cdot CO\cdot C_6H_3MeCl,$$

m. p. 90°, from which by means of nitric acid two *chlorodinitrotoluic acids*, m. p. 223° and 187—191° respectively, are obtained, the orientations of which are being investigated. The halogen is easily replaced by aniline, yielding yellow diphenylamine derivatives,

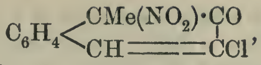
$$NHPh\cdot C_6HMe(NO_2)_2\cdot CO_2H,$$

m. p. 174° and 216° respectively. C. S.

Keto-chlorides of 1-Methyl-β-naphthol and their Relation to β-Naphthaquinols. Karl Fries and E. Hempelmann (*Ber.*, 1908, **41**, 2614—2626).—When chlorine is passed into a solution of 1-methyl-β-naphthol in slightly diluted acetic acid at 0°, 1-*chloro*-2-*keto*-1-*methyldihydronaphthalene*,  $C_6H_4<\begin{matrix}CMeCl\cdot CO\\ CH{=\!=}CH\end{matrix}$, is ultimately obtained as a colourless oil, which cannot be distilled without decomposition, is reduced again to 1-methyl-β-naphthol by stannous chloride, and dissolves in concentrated sulphuric acid with a yellow colour quickly becoming brown. By the use, alternately, of chlorine and of sodium acetate and acetic acid, the following compounds have been obtained in succession: 1 : 3 : 4-*trichloro*-2-*keto*-1-*methyltetrahydronaphthalene*, m. p. 78°; 1 : 3-*dichloro*-2-*keto*-1-*methyldihydronaphthalene*; 1 : 3 : 3 : 4-*tetrachloro*-2-*keto*-1-*methyltetrahydronaphthalene*, m. p. 124—125°; 1 : 3 : 4-*trichloro*-2-*keto*-1-*methyldihydronaphthalene*, m. p. 85°, and 1 : 3 : 3 : 4 : 4-*pentachloro*-2-*keto*-1-*methyltetrahydronaphthalene*, m. p. 105°. Of these compounds, the second and fourth resemble 1-chloro-2-keto-1-methyldihydronaphthalene in their behaviour with concentrated sulphuric acid, and all three dihydronaphthalene compounds may be regarded as the hydrochloric acid esters of 1-methyl-2-naphthaquinol, which shows similar colour reactions. The tetrahydronaphthalene derivatives are stable towards sulphuric acid.

The relation of the preceding derivatives of dihydronaphthalene to the 1-methyl-2-naphthaquinols has been further shown by taking advantage of the reactivity of the chlorine atom in position 1. All three derivatives react with silver acetate to form the corresponding methylnaphthaquinyl acetates, whilst, in addition, 1 : 3 : 4-trichloro-2-keto-1-methyldihydronaphthalene yields 3 : 4-*dichloro*-1-*methyl*-2-*naphthaquinol*,  $C_6H_4<\begin{matrix}C(Me\cdot OH)\cdot CO\\ CCl{=\!=\!=}CCl\end{matrix}$, when warmed in benzene solution with silver nitrite, and the *methoxy*-derivative, m. p. 90°, by treatment with sodium methoxide.

3-*Chloro*-1-*methyl*-β-*naphthol*, $C_{10}H_5MeCl\cdot OH$, m, p. 60°, obtained by the reduction of 1 : 3-dichloro-2-keto-1-methyldihydronaphthalene by stannous chloride, forms an *acetate*, m. p. 86°, and regenerates the dichloroketo-chloride by treatment with the calculated amount of chlorine in glacial acetic acid. 3 : 4-*Dichloro*-1-*methyl*-β-*naphthol*, m. p. 132°, obtained by the reduction of 1 : 3 : 4-trichloro-2-keto-1-methyldihydronaphthalene, forms an *acetate*, m. p. 96°.

3-*Chloro*-1 : 2-*methylnaphthaquinitrole*,  $C_6H_4<\begin{array}{l}CMe(NO_2)\cdot CO\\ |\\ CH{=\!=\!=\!=}CCl\end{array}$, m. p. 85—86° (decomp. just above m. p.), is obtained by passing nitrous fumes into ethereal 3-chloro-1-methyl-β-naphthol at 0°. 3 : 4-*Dichloro*-1 : 2-*methylnaphthaquinitrole*, m. p. 103—104° (decomp.), is obtained in a similar manner. The two compounds are remarkably stable towards dilute sodium carbonate or alcohol, but by prolonged heating in benzene or glacial acetic acid are converted into 3-*chloro*-1 : 2-*methylnaphthaquinol*, m. p. 70° (*acetate*, m. p. 133°), and 3 : 4-*dichloro*-1 : 2-*methylnaphthaquinol*, m. p. 114° (*acetate*, m. p. 149°), respectively.

C. S.

Halochromism of Quinones. Kurt H. Meyer (*Ber.*, 1908, 41, 2568—2576).—Quinones combine with acids and also with certain metallic halides, forming additive compounds which have a much deeper colour than the original ketones (compare Kehrmann and Mattisson, Abstr., 1902, i, 229; Vorländer, Abstr., 1905, i, 792). The compounds are unstable, and are decomposed by water, yielding the original quinones. The following compounds are all red in colour: p-*benzoquinone stannic chloride*, $C_6H_4O_2,SnCl_4,C_6H_6$ and $C_6H_4O_2,SnCl_4$; *a-naphthaquinone antimony pentachloride*, $C_{10}H_6O_2,2SbCl_5$; *anthraquinone antimony pentachloride*, $C_{14}H_8O_2,2SbCl_5$; *phenanthraquinone mercuric chloride*, $2C_{14}H_8O_2,HgCl_2$; *phenanthraquinone zinc chloride*, $C_{14}H_8O_2,ZnCl_2$; *phenanthraquinone ferric chloride*, $3C_{14}H_8O_2,FeCl_3$. Phenanthraquinone also forms a red additive *compound* with sulphur dioxide at about −50°.

The following compounds have a green colour: *phenanthraquinone stannic chloride*, $C_{14}H_8O_2,SnCl_4$, which turns red on exposure to the air; *phenanthraquinone aluminium chloride*, $C_{14}H_8O_2,AlCl_3$. The absorption curves for chloroform solutions of the additive compounds of a quinone with an acid and with a metallic halide are very similar.

Ketones also form coloured additive compounds with metallic chlorides. *Benzophenone antimony pentachloride*, $COPh_2,2SbCl_5$, crystallises in yellow needles, and *benzil stannic chloride*, $C_{14}H_{10}O_2,SnCl_4$, in yellow plates.

Triphenylchloromethane absorbs hydrogen chloride at −60°, yielding a yellow additive *compound*, $CPh_3Cl,6HCl$; the bromo-derivative yields a similar compound with hydrogen bromide.

The introduction of halogen into the quinone molecule, as, for example, in tetrachloro-*o*- and -*p*-benzoquinone, inhibits the formation of additive compounds with metallic salts.

J. J. S.

Quinonoid Compounds. XVI. Two Forms of *o*-Quinones. Richard Willstätter and Fritz Müller (*Ber.*, 1908, 41, 2580—2586. Compare Abstr., 1905, i, 144; this vol., i, 475).—A colourless modification of *o*-benzoquinone is obtained when the oxidation of catechol is carried out rapidly (fifteen seconds) at low temperatures.

It is necessary to wash the silver oxide well and to dry it by means of acetone and ether. The colourless crystals are obtained when the filtered ethereal solution is mixed with light petroleum, or cooled to −15° to −20°. The ethereal solutions are green, but the crystals are colourless. The compound has quinonoid properties, but is extremely unstable, and is either transformed into the red modification or decomposes.

When the pure red compound is dissolved in ether and the solution cooled, a mixture of the colourless and red crystals is obtained, so that in the solution the two compounds are present in a state of equilibrium.

The ketonic formula $O{:}C_6H_4{:}O$ is assigned to the red compound, and the formula $C_6H_4{<}^{O}_{O}{>}$ to the colourless.

J. J. S.

The Claisen Condensation. II. Mechanism of the Reaction.

J. Bishop Tingle and Ernest E. Gorsline (*Amer. Chem. J.*, 1908, **40**, 46—88. Compare Abstr., 1907, i, 498).—The authors have carried out a number of experiments with the object of ascertaining the influence of change of conditions on the Claisen condensation between certain ketones and esters, and, hence, on the yield of diketone. The principal results obtained are as follows.

With camphor as the ketone, calcium or sodamide is practically useless as a condensing agent unless alcohol is added, and, even then, a relatively high temperature is required (compare Claisen, Abstr., 1905, i, 286).

The nature of the "solvent product," or the residue left after the distillation of the solvent, varies in different cases. With condensations between camphor and ethyl oxalate in presence of sodium or sodamide, considerable quantities of camphoroxalic acid can be extracted from the solvent product, and the same holds when camphor and ethyl cinnamate are condensed by means of either of these agents. When, however, calcium is used, no trace of the condensation product is found in the solvent product.

The reaction is markedly influenced by the nature of the ketone or aldehyde employed, and also by that of the ester, and this influence is probably not confined to the velocity, but, in some cases, extends to the actual mechanism of the reaction. The readiness with which the reaction takes place is increased by the proximity of two carbethoxyl groups, and there are indications that the mechanism of the reactions resulting in the formation of diketones varies in the two cases of aliphatic and aromatic esters.

Experiments on the acetoacetic ester condensation, in which small quantities of ether, light petroleum, or pyridine were used as solvents, show that the catalytic influence of ether and pyridine on the velocity of the reaction is appreciable. No evidence could be obtained to show that ether or a tertiary base has any catalytic action when sodium reacts with esters to form compounds of the class

$$ONa\cdot CPh{:}CPh\cdot ONa.$$

It seems probable that the two reactions take place simultaneously, and that in the presence of solvents the reaction $2CH_3\cdot CO_2Et + 4Na = ONa\cdot CMe{:}CMe\cdot ONa + 2NaOEt$ preponderates considerably.

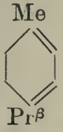
If the explanation of the Claisen condensation given by its discoverer (Abstr., 1895, i, 62) is correct, sodium ethoxide should be an excellent accelerator, and this is found to be the case, the addition of a little alcoholic sodium ethoxide accelerating to a marked degree the reactions between camphor and the esters of various acids in presence of light petroleum as solvent. Absolute alcohol is a still more effective accelerating agent, but sodium ethoxide free from alcohol affects the speed of the reaction very little, if at all. A striking fact is the very great reduction in the yield of diketone occurring when alcohol or alcoholic sodium ethoxide is added.

When the esters of the aliphatic series are condensed with camphor, the use of more than one atomic proportion of sodium does not increase the yield of the diketone. The catalytic agent does not accelerate the reaction between sodium and the ester, or that between sodium and camphor. Sodium camphor acts as a feeble condensing agent.

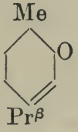
The authors' results indicate that, taken in connexion with the action of sodium on esters and with the catalytic influence of ether and the tertiary bases, Michael's explanation of the Claisen condensation (Abstr., 1901, i, 123; 1905, i, 506) is the most satisfactory.

T. H. P.

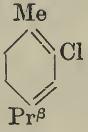
Constitution of Terpinene. CARL D. HARRIES and RIKO MAJIMA (*Ber.*, 1908, 41, 2516—2529).—Amenomija (Abstr., 1905, i, 803) suggested that carvenene (I) might be identical with terpinene, and attempted to prepare it from carvenone (II) in the same manner as Harries and Johnson obtained α-phellandrene (IV) from Δ^6-menthene-2-one (V), but was unable to reduce the intermediate chloro-compound (III).



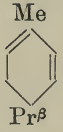
(I.)



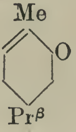
(II.)



(III.)

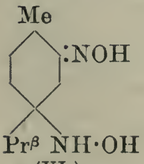


(IV.)

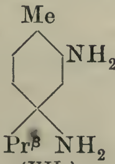


(V.)

It is now found that when carvenone is converted by way of its oxime into 2-amino-Δ^3-menthene, and the phosphate of this base is distilled, a single hydrocarbon, which must be carvenene, is obtained, but if the ketone is converted into its hydroxylamino-oxime (VI), and this into 2:4-diaminomenthane (VII), distillation of the phosphate leads to the formation of a mixture of hydrocarbons.



(VI.)



(VII.)

The relation of carvenone to terpinene is discussed (compare Wallach, Abstr., 1907, i, 64; Semmler, Abstr., 1907, i, 714).

Carvenone forms two oximes, one of which, m. p. 90—92° (Wallach, Abstr., 1894, i, 44; 1895, i, 672), forms a hydrochloride, m. p. 113—114°, crystallising from ether-alcohol. The other *oxime* is an oil, and forms a *hydrochloride*, m. p. 105—113°, which remains dissolved in the ether-alcoholic mother liquor. Reduction of carvenoneoxime with zinc dust in acetic acid solution leads to the formation of the *imine*, which is isolated as the crystalline *oxalate*,

$$C_{10}H_{17}N,2C_2H_2O_4;$$

this is readily hydrolysed by water, forming ammonium oxalate and carvenone. The free imine, b. p. 105°/12 mm., decomposes at the ordinary temperature, and yields benzamide when benzoylated by the Schotten-Baumann method. Contrary to Wallach and Boedecker's statement (Abstr., 1907, i, 943), carvenoneoxime cannot be formed intermediately in the reduction of terpinene nitrosite, as, although hydrolysed by sulphuric acid, it is stable towards boiling glacial acetic acid.

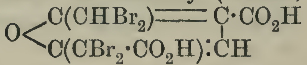
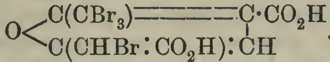
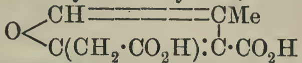
2-*Amino*-Δ^3-*menthene* (*carvenylamine*), $C_{10}H_{19}N$, prepared by reduction of carvenoneoxime by means of aluminium amalgam in ethereal solution, is separated from the imine formed simultaneously by hydrolysis of the latter with hydrochloric acid. It has b. p. 86—89°/10 mm., D_4^{20} 0·8762, and n_D^{20} 1·46966. When boiled with acetic anhydride, it forms a *syrup*, which decolorises bromine. The *benzoyl* and *phenylcarbamide* derivatives are syrups. The *hydrochloride*, *nitrate*, and *acid oxalate*, m. p. about 120°, are described.

Carvenene ($\Delta^{1,3}$-*menthadiene*), $C_{10}H_{16}$, b. p. 68—70°/15 mm., D_4^{18} 0·8453, n_D^{18} 1·48579, prepared by distillation of carvenylamine phosphate, has a faint odour of lemons, and forms terpinene nitrosite, m. p. 155—156°.

Carvenone hydroxylamino-oxime, prepared from dihydrocarvone or from terpinene nitrosite, has m. p. 162—162·5° (167—168°: Tiemann and Semmler, Abstr., 1899, i, 224), and when treated with mercuric oxide forms the *nitroso-oxime*, $C_{10}H_{18}O_2N_2$, blue crystals, m. p. 113—115°, together with a white, sparingly soluble, crystalline *substance*.

2 : 4-*Diaminomenthane*, $C_{10}H_{22}N_2$, prepared by reduction of the hydroxylamino-oxime with sodium and alcohol, is an oil, b. p. 121·5°/12 mm., D_4^{20} 0·9192, n_D^{20} 1·4848. The *hydrochloride*, *sulphate*, *nitrate*, *platinichloride*, *oxalate*, *benzoyl* derivative, and *phenylcarbamide* derivative, m. p. 220—222°, are described. On distillation, the phosphate of the diamine yields a mixture of hydrocarbons, b. p. 62—65°/11 mm., D_4^{17} 0·8611, n_D^{17} 1·48802, which gradually forms a syrup. The fresh mixture yields small amounts of terpinene nitrosite. The action of sodium nitrite on the diamine hydrochloride leads to the formation of an *oil*, b. p. 65—100°/12 mm., which does not yield terpinene nitrosite. G. Y.

Components of Ethereal Oils. Elimination of Methoxy-groups in the para-Position with Respect to Allyl or Propenyl Radicles. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 2556—2557. Compare this vol., i, 557, 558, 664).—The product obtained by reducing elemicin or, even better, *iso*elemicin with sodium and alcohol is shown to have the composition $C_{11}H_{16}O_2$, and is 3 : 5-*dimethoxy*-1-n-*propylbenzene*, since it yields 3 : 5-dimethoxybenzoic acid when oxidised. The reduction thus consists in the conversion of the propenyl to a propyl group, and the elimination of the methoxy-radicle which was in the para-position with respect to the propenyl group. The propenyl group thus behaves in much the same manner as the keto-group (compare Kostanecki, this vol., i, 359). J. J. S.

Position of Bromine Atoms in Derivatives of Methronic Acid. Hypolyt Trephilieff (*Ber.*, 1908, 41, 2543—2544).—The tetrabromo-derivative of methronic acid described recently (Abstr., 1907, i, 1063) may have the constitution (I)  $O<\begin{matrix}C(CHBr_2)=\!=\!=C\cdot CO_2H\\ C(CBr_2\cdot CO_2H):CH\end{matrix}$ or (II)  $O<\begin{matrix}C(CBr_3)=\!=\!=\!=C\cdot CO_2H\\ C(CHBr:CO_2H):CH\end{matrix}$. It is now found that the action of bromine on ethyl phenithronate leads to the formation of a *dibromo*-derivative, $C_{15}H_{12}O_3Br_2$, which is obtained in yellow crystals, and on 3-carboxy-2-methylfuran-4-acetic acid,  $O<\begin{matrix}CH=\!=\!=\!=\!=CMe\\ C(CH_2\cdot CO_2H):C\cdot CO_2H\end{matrix}$ (Feist, Abstr., 1899, i, 675), to that of a *tribromo*-derivative, $C_8H_5O_5Br_3$, which crystallises from acetic acid. Both these derivatives decompose without melting when heated. Bromine does not react, on the other hand, with the methyl groups of 3 : 4-dimethylfurandicarboxylic acid; hence it is considered that the tetrabromo-derivative of methronic acid has the constitution (I). G. Y.

Constitution of Methronic Acid. Hypolyt Trephilieff (*Ber.*, 1908, 41, 2545—2546. Compare Abstr., 1906, i, 528).—The fraction, b. p. 300—305°, obtained from the product of the action of sodium succinate on ethyl acetoacetate (Fittig and Hantzsch, Abstr., 1889, 126), contains ethyl methronate, which on hydrolysis yields methronic acid. This, when treated with aqueous ammonia at 320°, forms dimethylpyrrole, b. p. 165°.

When exposed to bromine vapour for two to three months, 2 : 5-dimethylfuran-3-carboxylic acid forms a *tetrabromo*-derivative, $C_7H_4O_3Br_4$, which is obtained as a crystalline mass. G. Y.

Crystallography of the Fulgides. Zoltán Toborffy (*Zeitsch. Kryst. Min.*, 1908, 45, 155—181).—Crystallographic details are given concerning thirty-nine fulgide compounds recently prepared by Stobbe (Abstr., 1905, i, 857; 1906, i, 960). L. J. S.

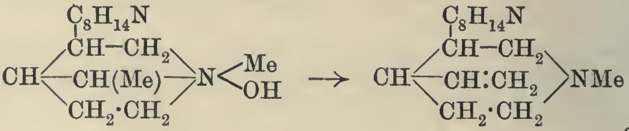
Reactions of Hordenine Based on the Constitution of this Substance. Georges Denigès (*Bull. Soc. chim.*, 1908, [iv], 3, 786—792).—The constitution assigned by Léger to this alkaloid (Abstr., 1906, i, 204, 761; 1907, i, 151, 234, 337) indicates that it contains residues of *p*-cresol and of trimethylene, and the following reactions characteristic of substances containing these residues confirm Léger's formula.

When a drop of a solution of hordenine sulphate is placed on a glass slip and a drop of iodine solution is added, characteristic crystals of a brown iodo-compound separate, which are visible under the microscope. Trimethylamine yields a crystalline derivative under the same conditions, as does also choline.

Hordenine (0·02—0·03 gram) dissolved in 4 c.c. of acetic acid gives, on boiling with four drops of formaldehyde solution and the subsequent addition of 3 c.c. of sulphuric acid, a green coloration, which rapidly deepens. Tyrosine, under the same conditions, gives a red coloration, which, on gently warming, passes into green. Under somewhat similar conditions, *p*-cresol also gives a green coloration. Similar green colorations are obtained with tyrosine or hordenine when formaldehyde solution is replaced by paraldehyde. Precise instructions for the application of these tests under various conditions are given in the original. It is suggested that Aloy and Rabaut's tyrosine colour reaction with bromine and ammonia solution (this vol., i, 341) is probably due to the presence of the *p*-cresol residue. *p*-Cresol gives with bromine water, followed by ammonia, a yellow coloration, passing into orange, and hordenine an intense yellow.

T. A. H.

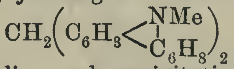
Sparteine. Transformation of *iso*Sparteine into α-Methylsparteine. AMAND VALEUR (*Compt. rend.*, 1908, 147, 127—129. Compare this vol., i, 43, 44, 103, 206).—When the solution of α-methylsparteine, after isomerisation by boiling with dilute sulphuric acid, is evaporated in a vacuum, crystals of iso*sparteine methosulphate*, $C_{15}H_{26}N_2Me,HSO_4,9H_2O$, are formed, having $[\alpha]_D$ −13·65°. This salt is decomposed by baryta with the formation of *α-methyl*iso*sparteinium hydroxide,* which yields a precipitate of *iso*sparteine methiodide with potassium iodide, and is quantitatively transformed into α-methylsparteine by heating in a vacuum below 100°. Adopting the author and Moureu's constitutional formula for sparteine, the last change may be represented thus:



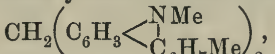
G. B.

Organic and Fused Salts (Conductivity). CARL SCHALL (*Zeitsch. Elektrochem.*, 1908, 14, 397—405).—*Quinoline* n-*butiodide*, m. p. 175·5—176·1°, and iso*butiodide,* m. p. 159—159·5°, were prepared. The following salts were also prepared in a very pure state: Pyridine methiodide dibromide, m. p. 68—69°; quinoline hydriodide di-iodide, m. p. 67°; quinoline methiodide di-iodide, m. p. 108·6—109·6°; quinoline methiodide tetra-iodide, m. p. 72—73°; quinoline ethiodide di-iodide, m. p. 43—45°; quinoline propiodide di-iodide, m. p. 60°; quinoline *n*-butiodide di-iodide, m. p. 60·7°, and quinoline *iso*butiodide di-iodide, m. p. 85·6°. The *iso*propyl salt could not be obtained pure. The di-iodides of the hydriodides and methiodides show slight dissociation at their melting points; the other salts evolve mere traces of iodine or none. The electrical conductivity of the *n*-propyl, *n*-butyl, and *iso*butyl compounds was measured for the fused anhydrous substances at several temperatures.

T. E.

Dihydrazines. II. Diphenylmethanedimethylhydrazine and Cyclic Ketones. Julius von Braun (*Ber.*, 1908, 41, 2604—2607. Compare this vol., i, 700).—*cyclo*Hexanone (2 mols.) reacts with an acetic acid solution of diphenylmethanedimethyldihydrazine (1 mol.) in the presence of a little sulphuric acid, yielding the *bistetrahydrodicarbazole* of the diphenylmethane series,  $\mathrm{CH_2}\left(\mathrm{C_6H_3}<\begin{matrix}\mathrm{NMe}\\ |\\ \mathrm{C_6H_8}\end{matrix}\right)_2$ It is best purified by solution in pyridine and precipitation with alcohol, has m. p. 175°, and dissolves in concentrated acids.

1-Methyl*cyclo*hexan-4-one yields a similar derivative,



$$\mathrm{CH_2}\left(\mathrm{C_6H_3}<\begin{matrix}\mathrm{NMe}\\ |\\ \mathrm{C_6H_7Me}\end{matrix}\right)_2,$$

m. p. 143°, and the corresponding *m*-compound, an isomeride, m. p. 200°.

1-Methyl*cyclo*hexan-2-one, menthone, 1 : 3-dimethyl*cyclo*hexen-5-one, and sabinaketone do not react with diphenylmethanedimethyldihydrazine. It thus appears that only those cyclic ketones which contain the grouping $\cdot\mathrm{CH_2}\cdot\mathrm{CO}\cdot\mathrm{CH_2}\cdot$ are capable of reacting with the dihydrazine.

*cyclo*Pentanone does not react so readily as *cyclo*hexanone, and does not yield a pure product. J. J. S.

Reduction of Phenylhydrazones in Alkaline Solution. Oskar Schlenk (*J. pr. Chem.*, 1908, [ii], 78, 49—63).—Whilst the action of sodium amalgam on phenylhydrazones in acid solution leads to the formation of amines, $\mathrm{R\cdot CH\colon N\cdot NHPh} \longrightarrow \mathrm{R\cdot CH_2\cdot NH_2 + NH_2Ph}$ (Tafel, Abstr., 1887, 975), the reduction in alkaline solution allows, in the case of phenylhydrazones of aromatic aldehydes, of the isolation of the intermediate hydrazine, $\mathrm{R\cdot CH_2\cdot NH\cdot NHPh}$. In the following alkaline reductions, part of the excess of sodium hydroxide was neutralised by a current of carbon dioxide.

β-Phenylbenzylhydrazine, $\mathrm{CH_2Ph\cdot NH\cdot NHPh}$, formed by the action of sodium amalgam on phenylbenzylidenehydrazine in boiling alcoholic solution, crystallises in colourless rhombohedra, m. p. 35°, b. p. 290° (decomp.) (m. p. 155·5°: Schlömann, Abstr., 1893, i, 452), reduces Fehling's solution when heated and silver solutions at the ordinary temperature, and, on exposure to air, changes into a yellow mass, from which phenylbenzylidenehydrazine gradually crystallises. The *hydrochloride*, $\mathrm{C_{13}H_{14}N_2,HCl}$, forms white leaflets, m. p. 205°; the *hydrogen oxalate*, $\mathrm{C_{15}H_{16}O_4N_2}$, m. p. 190°. The action of oxidising agents on β-phenylbenzylhydrazine leads to the formation of phenylbenzylidenehydrazine, and the prolonged action of mercuric oxide to that of the yellow tetrazone. On reduction with sodium amalgam and acetic acid, β-phenylbenzylhydrazine yields aniline and benzylamine. The *acetyl* derivative, $\mathrm{CH_2Ph\cdot NAc\cdot NHPh}$, prepared by adding the hydrazine to a cooled solution of zinc chloride in acetic anhydride, crystallises in prisms, m. p. 91°, reduces Fehling's solution only on prolonged boiling, and forms a *nitroso*-derivative, $\mathrm{CH_2Ph\cdot NAc\cdot NPh\cdot NO}$, crystallising in yellow rhombohedra, m. p. 84°. This gives Liebermann's reaction, and on reduction with zinc dust and acetic acid yields phenylhydrazine and acetylbenzylamine. The *benzoyl* derivative, $CH_2Ph\cdot NBz\cdot NHPh$, formed by the action of benzoyl chloride on the hydrazine in cooled ethereal solution, crystallises in colourless needles, m. p. 121—122°, and yields a *nitroso*-derivative, $C_{20}H_{17}O_2N_3$, crystallising in yellow needles, m. p. 102°. The *dibenzoyl* derivative, $CH_2Ph\cdot NBz\cdot NPhBz$, formed by the Schotten-Baumann method, crystallises in hexagonal prisms, m. p. 131°.

p-*Tolylbenzylidenehydrazine*, $C_{14}H_{14}N_2$, crystallises from alcohol in colourless needles, m. p. 125°, becomes intensely red on exposure to air, and on reduction with sodium amalgam in boiling alcoholic solution yields *β-p-tolylbenzylhydrazine*, $C_{14}H_{16}N_2$, which is obtained as a viscid, yellow oil, b. p. 212°/17 mm., reduces Fehling's solution when heated, and on exposure to air or when treated with oxidising agents again forms the hydrazone. The *hydrochloride*,

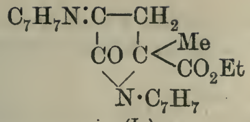
$$C_{14}H_{16}N_2,HCl,H_2O,$$

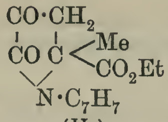
long, thin needles, m. p. 185° (decomp.), loses H_2O slowly in a vacuum. The *benzoyl* derivative, $C_{21}H_{20}ON_2$, crystallises in white needles, m. p. 159°.

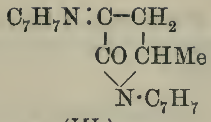
Reduction of the phenylhydrazone of benzylideneacetone by means of sodium amalgam and acetic acid in alcoholic solution leads to the formation of *γ-amino-α-phenylbutane*, $CH_2Ph\cdot CH_2\cdot CHMe\cdot NH_2$, which is obtained as a colourless oil, b. p. 222°/716 mm., D_4^{15} 0·9289, has a slight ammoniacal odour and a strong alkaline reaction, is only sparingly soluble in water, and absorbs carbon dioxide from the air, forming a crystalline *carbonate*. The *hydrochloride*, needles, m. p. 144°; the *platinichloride*, $(C_{10}H_{15}N)_2H_2PtCl_6$, yellow leaflets, decomp. 220°; the *sulphate*, m. p. 255° (decomp.); the *hydrogen oxalate*, m. p. 110°; the *oxalate*, m. p. 232°; the *benzoyl* derivative, needles, m. p. 107°. The action of sodium nitrite on the base in hot hydrochloric acid solution leads to the formation of α-phenyl-β-butylene and a product of high boiling point, which may be the corresponding alcohol or a polymeride of the butylene. When heated with sodium amalgam in alcoholic solution at 55°, the phenylhydrazone of benzylideneacetone yields the *phenylhydrazone* of benzylacetone, $C_{16}H_{18}N_2$, which crystallises in colourless leaflets, m. p. 59°, is unstable, changing to a reddish-yellow oil, and has slight basic properties.

The alkaline reduction of benzilosazone leads to the formation of diphenylhydroxyethylamine, diphenylethylenediamine, m. p. 107—110° (90—92°: Feist, Abstr., 1894, i, 196; 120°: Grossmann, Abstr., 1889, 1191), and tetraphenylpyrazine, m. p. 244°. G. Y.

Mechanism of the Synthesis of Cyclic Nitrogen Compounds. Action of Ethyl Pyruvate on *p*-Toluidine. Louis J. Simon (*Compt. rend.*, 1908, 147, 125—127. Compare this vol., i, 296, 687).—The ester, $C_{22}H_{24}O_3N_2$ (I), previously obtained by the interaction of *p*-toluidine and ethyl pyruvate, is hydrolysed by cold concentrated sulphuric acid to a *substance*, $C_{15}H_{15}O_4N$ (II), m. p. 152°, and is transformed by alcoholic potassium hydroxide into a *substance*, $C_{19}H_{20}ON_2$, m. p. 190°. The three substances may be represented thus:


(I.)


(II.)


(III.)

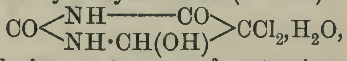
Simultaneously with the substance (I), there is also formed a more soluble *substance*, $C_{24}H_{30}O_4N_2$, m. p. 142°, which may be represented thus: $C_7H_7{\cdot}NH{\cdot}CMe(CO_2Et){\cdot}CH_2{\cdot}C(CO_2Et){:}N{\cdot}C_7H_7$, and is transformed by alcoholic potassium hydroxide into an *acid*, m. p. 265° (decomp.), in all probability 4 : 6-*dimethylquinoline*-2-*carboxylic acid*.

G. B.

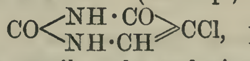
Action of Nitric Acid on 2 : 6-Dioxypyrimidines. Nitrohydroxyhydrothymine. XXX. TREAT B. JOHNSON (*Amer. Chem. J.*, 1908, **40**, 19—36. Compare this vol., i, 692).—The author has not been able to obtain Steudel's nitrothymine (Abstr., 1901, i, 434), which he regards as a secondary decomposition product, and not as a simple thymine derivative.

With fuming nitric acid (D 1·5) at the ordinary temperature, uracil gives 5-nitrouracil; 5-bromouracil, 5-bromo-5-nitro-4-hydroxyhydrouracil (compare Behrend, Abstr., 1887, i, 919); 5-chlorouracil, 5-chloro-5-nitro-4-hydroxyhydrouracil, and thymine, 5-nitro-4-hydroxyhydrothymine. The formation of these hydropyrimidines involves a direct addition of nitric acid to the double linking between the 4- and 5-positions of the pyrimidine ring (compare Behrend, *Annalen*, 1885, **229**, 1—44).

The reduction of 5-bromo-5-nitro-4-hydroxyhydrouracil by means of tin and hydrochloric acid yields Behrend's hydroxyxanthine (*loc. cit.*).

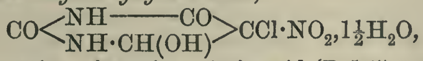


5 : 5-*Dichloro*-4-*hydroxyhydrouracil*, $CO{<}\begin{matrix}NH\text{———}CO\\ NH{\cdot}CH(OH)\end{matrix}{>}CCl_2,H_2O$, prepared by the action either of chlorine water or of potassium chlorate and hydrochloric acid on uracil, crystallises from water in large prisms, m. p. 212—215° (decomp.).



5-*Chlorouracil*, $CO{<}\begin{matrix}NH{\cdot}CO\\ NH{\cdot}CH\end{matrix}{\geqslant}CCl$, prepared by the action of chlorine water on uracil or by reducing the preceding compound by means of tin and hydrochloric acid, crystallises from water in prisms, m. p. 300—305°.

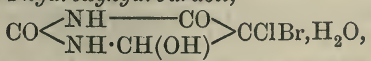
5-*Chloro*-5-*nitro*-4-*hydroxyhydrouracil*,



$$CO{<}\begin{matrix}NH\text{———}CO\\ NH{\cdot}CH(OH)\end{matrix}{>}CCl{\cdot}NO_2,1\tfrac{1}{2}H_2O,$$

obtained by the action of fuming nitric acid (D 1·5) on 5-chlorouracil, separates in hard, prismatic crystals, which decompose with effervescence at 150—160°.

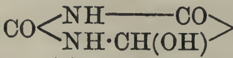
5-*Chloro*-5-*bromo*-4-*hydroxyhydrouracil*,



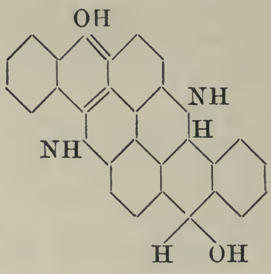
$$CO{<}\begin{matrix}NH\text{———}CO\\ NH{\cdot}CH(OH)\end{matrix}{>}CClBr,H_2O,$$

prepared from 5-bromouracil or 5-chlorouracil by the action of chlorine or bromine water respectively, crystallises from bromine water in prisms, decomposing with effervescence at 195—200°, and yields 5-chlorouracil when boiled with alcohol.

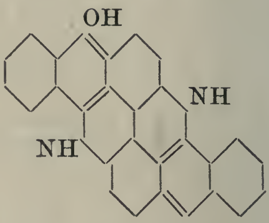
The action of bromine water on 5-iodouracil yields 5 : 5-dibromo-4-hydroxyhydrouracil (compare Wheeler and Johnson, Abstr., 1907, ii, 826).

5-*Nitro-4-hydroxyhydrothymine*,  $CO<\begin{matrix}NH\text{———}CO\\NH\cdot CH(OH)\end{matrix}>CMe\cdot NO_2$, exists in the following two modifications: (1) the *α-form*, obtained by dissolving thymine in fuming nitric acid, separates in triclinic prisms or blocks [W. E. Ford: $a:b:c=0{\cdot}578:1:0{\cdot}420$; $\alpha=107°35'$, $\beta=100°25'$, $\gamma=80°59'$], m. p. 183° (decomp.), and dissolves in water, giving an acid solution, or in alcohol. (2) The β- or unstable *modification*, obtained under certain conditions when thymine is dissolved in fuming nitric acid, crystallises from water or alcohol in prisms, m. p. 230—235°, and gradually changes into the β-form when kept at the ordinary temperature. Both modifications yield thymine when reduced with tin and hydrochloric acid. T. H. P.

Indanthren and Flavanthren. XI. Reduction Products of Flavanthren. Roland Scholl and W. Neovius (*Ber.*, 1908, 41, 2534—2540. Compare this vol., i, 696).—Energetic reduction of flavanthren with zinc dust and sodium hydroxide leads to the formation of α-hexahydroflavanthren (I) and flavanthrinol (II):



(I.)

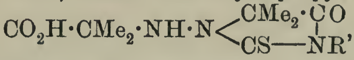


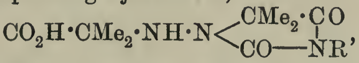
(II.)

α-Hexahydroflavanthren hydrate is obtained as a stable, blackish-blue powder, $C_{28}H_{18}O_2N_2,H_2O$, which loses H_2O at 160°, dissolves in alcohol to a bluish-red, or if highly dilute to a violet, solution with brilliant, scarlet fluorescence, but in nitrobenzene to a non-fluorescent solution, forms fluorescent solutions in alcoholic alkalis or concentrated acids, and dyes unmordanted wool in an alkaline bath red, becoming greenish-blue on treatment with acids, and violet with water. On prolonged heating with zinc dust in alkaline solution, α-hexahydroflavanthren hydrate is converted into flavanthrinol hydrate, whilst the anhydrous hexahydro-compound forms anhydrous flavanthrinol when heated at 300° in a current of carbon dioxide. On treatment with a current of air in alkaline solution, the hexahydro-compound is oxidised to flavanthren.

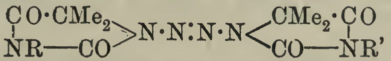
Flavanthrinol hydrate, $C_{28}H_{16}ON_2,H_2O$, forms a blue, voluminous precipitate, becoming blackish-blue when dried, loses H_2O at 160°, is less soluble than α-hexahydroflavanthren hydrate, forms red solutions with olive-green fluorescence in organic solvents, except nitrobenzene, in which it is not fluorescent, gives coloured solutions with reddish-brown fluorescence in concentrated acids, and dyes unmordanted wool violet-red, becoming green with acids, and blue with water. Flavanthrinol is not oxidised by air at the ordinary temperature, but, on treatment with ferricyanide or when heated in air, yields flavanthren.

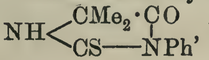
G. Y.

Desulphurisation of Thiohydantoins. James R. Bailey and C. P. Randolph (*Ber.*, 1908, 41, 2494—2505).—Bailey observed (Abstr., 1904, i, 826) that 1-carboxy*iso*propylamino-5 : 5-dimethyl-2-thiohydantoins,  $CO_2H\cdot CMe_2\cdot NH\cdot N<\begin{array}{l}CMe_2\cdot CO\\ CS—NR\end{array}$, having R = an alphyl or aryl group in position 3, are readily converted by means of mercuric oxide into the corresponding hydantoins,



$$CO_2H\cdot CMe_2\cdot NH\cdot N<\begin{array}{l}CMe_2\cdot CO\\ CO—NR\end{array},$$

which on treatment with bromine water are oxidised, forming the azo-compounds,  $\begin{array}{l}CO\cdot CMe_2\\ NR—CO\end{array}>N\cdot N{:}N\cdot N<\begin{array}{l}CMe_2\cdot CO\\ CO—NR\end{array}$, containing the tetrazone grouping $\cdot N\cdot N{:}N\cdot N\cdot$. It is found now that the desulphurisation and the oxidation to the tetrazone take place in one operation when the thiohydantoin is treated with bromine water. These observations led to the study of the desulphurisation of thiohydantoins in general. Although the statements of Aschan (Abstr., 1884, 907) and of Marckwald, Neumark, and Stelzner (Abstr., 1892, 149) suggest that this desulphurisation takes place with ease, it is found that the thiohydantoins studied other than those already mentioned are not converted into hydantoins by the action of mercuric oxide. On the other hand, the desulphurisation does take place readily when the alkali salts of the thiohydantoic acids are treated with mercuric oxide, the resulting hydantoates being readily converted into the hydantoins. Thus 3-methylhydantoin and 3-ethylhydantoin are formed by heating potassium methylthiohydantoate and ethylthiohydantoate respectively with mercuric oxide in aqueous solution.

Whilst 1-carboxy*iso*propylamino-3-phenyl-5 : 5-dimethyl-2-thiohydantoin is readily desulphurised by mercuric oxide, 3-phenyl-5 : 5-dimethylhydantoin is not obtained by the action of mercuric oxide on the thiohydantoin,  $NH<\begin{array}{l}CMe_2\cdot CO\\ CS—NPh\end{array}$, but, on the other hand, all thiohydantoins derived from α-amino*iso*butyric acid are desulphurised normally by bromine water. Thiohydantoins derived from glycine or alanine, that is, containing one or two hydrogen atoms in position 5, when treated with bromine water, yield sulphuric acid and halogen-substitution products of the hydantoins (compare Andreasch, Abstr., 1902, i, 157).

Ethylhydantoic acid, $C_5H_{10}O_3N_2$, prepared from the hydantoin, has m. p. 132° (decomp.).

3-*Allylhydantoin*, $C_6H_8O_2N_2$, crystallises in thin needles, m. p. 78°.

3-p-*Tolylhydantoic acid*, $C_{10}H_{12}O_3N_2$, separates from alcohol in crystals, m. p. 203° (decomp.); the *ethyl* ester, m. p. 166°. 3-*p*-Tolyl-hydantoin crystallises in needles, m. p. 211° (205°: Quenda, Abstr., 1892, 828).

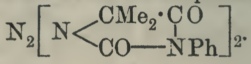
Phenylmethylhydantoic acid, prepared by the action of mercuric oxide on the corresponding potassium thiohydantoate, has m. p. 170° (decomp.), and on treatment with acids is converted into 3-phenyl-5-methylhydantoin.

The following hydantoins were prepared by the action of bromine water on the corresponding thiohydantoins, sulphuric acid being formed to the extent of about 66% of the theoretical amount. The thiohydantoins were formed from α-amino*iso*butyronitrile by Marckwald, Neumark, and Stelzner's method (*loc. cit.*). The data in brackets after the m. p.'s are those given by Marckwald, Neumark, and Stelzner.

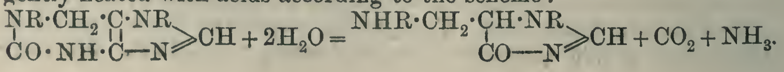
3-Phenyl-5 : 5-dimethylthiohydantoin crystallises in prisms, m. p. 174° (67°); the methyl ether, $C_{11}H_{11}ON_2\cdot SMe$, m. p. 96° (viscid liquid), forms a platinichloride, $(C_{12}H_{14}ON_2S)_2H_2PtCl_6$, decomp. about 240° (132°), and a picrate, $C_{12}H_{14}ON_2S,C_6H_3O_7N_3$, m. p. 194° (174°). 3-*Phenyl*-5 : 5-*dimethylhydantoin*, $C_{11}H_{12}O_2N_2$, crystallises in broad prisms, m. p. 171°, and is obtained also from α-amino*iso*butyronitrile and phenylcarbimide.

3 : 5 : 5-Trimethylthiohydantoin, $C_6H_{10}ON_2S$, crystallises in microscopic prisms, m. p. 145° (53°), and appears to form a sparingly soluble *compound* with mercuric oxide, blackening not taking place. 3 : 5 : 5-*Trimethylhydantoin*, $C_6H_{10}O_2N_2$, crystallises in long prisms, m. p. 149°.

3-*p*-Tolyl-5 : 5-dimethylthiohydantoin, $C_{12}H_{14}ON_2S$, forms needles, m. p. 223° (85°). 5-p-*Tolyl*-5 : 5-*dimethylhydantoin*, $C_{12}H_{14}O_2N_2$, m. p. 175°. G. Y.

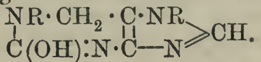
Thiohydantoins and Bases derived from These. JAMES R. BAILEY and C. P. RANDOLPH (*Ber.*, 1908, **41**, 2505—2508).—The authors draw attention to, and discuss some possible explanations of, the differences in the properties of the thiohydantoins described by Marckwald, Neumark, and Stelzner (Abstr., 1892, 149), and of those prepared by the same methods by themselves (preceding abstract). The constitution of the thiohydantoins now obtained is confirmed by the conversion of 3-phenyl-5 : 5-dimethyl-2-thiohydantoin into 3-phenyl-5 : 5-dimethylhydantoin, which is formed also by condensation of α-amino*iso*butyronitrile with phenylcarbimide, and by the action of sulphuric acid on 1-azo-3-phenyl-5 : 5-dimethylhydantoin,  $N_2\left[N<\begin{matrix}CMe_2\cdot CO\\ |\\ CO—NPh\end{matrix}\right]_2$. G. Y.

Hydrolysis of Xanthines and Deoxyxanthines. JULIUS TAFEL and RUDOLF MAYER (*Ber.*, 1908, **41**, 2546—2556. Compare Abstr., 1907, i, 984).—It has been observed that, whilst some deoxyxanthines decompose readily with evolution of carbon dioxide when heated with dilute acids, others exhibit much greater stability. A systematic study has now shown that xanthine itself and all methylated xanthines which are not methylated in position 3 are readily hydrolysed when gently heated with acids according to the scheme:



$$\begin{matrix}NR\cdot CH_2\cdot C\cdot NR\\ |\qquad\quad ||\\ CO\cdot NH\cdot C—N\end{matrix}\!\!>CH + 2H_2O = \begin{matrix}NHR\cdot CH_2\cdot CH\cdot NR\\ |\\ CO—N\end{matrix}\!\!>CH + CO_2 + NH_3.$$

Thus, under the same conditions, deoxyxanthine, deoxyheteroxanthine, and deoxyparaxanthine form 5-aminomethyl-4-iminazolones and evolve carbon dioxide, with similar velocities. On the other hand, 3-methylxanthine, theobromine, theophylline, and caffeine are much more stable towards acids, and when hydrolysed undergo more complicated reactions, which do not yield definite products. It is suggested that the ready and simple hydrolysis depends on the possibility of the deoxyxanthine reacting in the tautomeric form



$$\left.\begin{array}{l} NR\cdot CH_2\cdot C\cdot NR \\ C(OH):N\cdot C\text{—}N \end{array}\right> CH.$$

Tables are given showing the results of determinations of the rate of hydrolysis of deoxyxanthine, deoxyheteroxanthine, and deoxyparaxanthine, as measured by the carbon dioxide evolved and by the ammonia formed. The 5-aminomethyl-4-iminazolones, formed by the acid hydrolysis of the deoxyxanthines, are strongly basic, amorphous substances, readily soluble in water, and are unstable, but form stable, crystalline salts.

5-*Aminomethyl*-1-*methyl*-4-*iminazolone*, from deoxyheteroxanthine, is isolated as the *hydrochloride*, $C_5H_9ON_3,HCl$, which crystallises in needles, decolorises bromine water, and gives an odour of *iso*nitrile when heated with chloroform and alcoholic potassium hydroxide. The *platinichloride*, $(C_5H_{18}ON_3)_2H_2PtCl_6$, yellowish-red needles; the *picrate*, $C_{11}H_{12}O_8N_6$, yellow needles. 5-*Aminomethyl*-4-*iminazolone hydrochloride*, $C_4H_7ON_3,HCl$, from deoxyxanthine, and 5-*methylaminomethyl*-1-*methyl*-4-*iminazolone hydrochloride*, $C_6H_{11}ON_3,HCl$, from deoxyparaxanthine, were analysed.

The hydrolysis of the deoxyxanthines by baryta also has been studied and compared with that of the xanthines. From Fischer's results (Abstr., 1899, i, 262), it was to be expected that the rate of hydrolysis would be related directly to the acidity of the xanthine (Wood, Trans., 1906, **89**, 1839). The results now obtained with xanthine, 3-methylxanthine, heteroxanthine, theophylline, paraxanthine, theobromine, and caffeine, and with the corresponding deoxy-compounds, show that this is not the case with either class of substance. Moreover, the rule that the ease of hydrolysis increases with the number of methyl groups, to which the behaviour of the xanthines approximates, does not hold good for the deoxyxanthines.

G. Y.

Brominations by means of Diazobenzene Perbromides. Carl Bülow and Hermann Schmachtenberg (*Ber.*, 1908, **41**, 2607—2614).—When diazobenzene perbromide is dissolved in well-cooled acetone or acetophenone and the temperature allowed to rise, a vigorous reaction begins at 14·9°, hydrogen bromide is evolved, crystals of diazobenzene bromide separate, and a monobromo-derivative of the ketone is formed. When the perbromide is kept for some four to five days, decomposition occurs, phenol and tribromophenol being formed according to the equation: $3PhN_2Br_3 + 3H_2O \longrightarrow C_6H_2Br_3\cdot OH + 2PhOH + 6HBr + 3N_2$. Unsaturated compounds can also be converted into dibromides by the action of an acetic acid solution of the perbromide. Cinnamic acid, ethyl cinnamate, and phenylpropiolic acid have been brominated in this manner.

Acetyl-*p*-aminodiazobenzene perbromide (Silberrad and Smart, Trans., 1906, **89**, 170) is much more stable than diazobenzene perbromide, and gives up bromine only when kept for several weeks in a moist atmosphere. The corresponding *acetyl*-p-*aminodiazobenzene bromide*, $NHAc{\cdot}C_6H_4{\cdot}N_2{\cdot}Br$, is also stable, m. p. 116°. It may be kept in a desiccator over calcium chloride; it is readily soluble in water, and is very slowly decomposed by water at the ordinary temperature. The perbromide of the acetyl derivative also acts as a brominating agent. J. J. S.

Hydrolysis of Vignin. Thomas B. Osborne and Frederick W. Heyl (*Amer. J. Physiol.*, 1908, **22**, 362—372).—Vignin is the name given to the principal protein of the seeds of the cow-pea (*Vigna sinensis*); it is a globulin freely soluble in a 5% solution of sodium chloride, and nearly insoluble in a 1% solution of the same salt. The yield of cleavage products brought about by acid hydrolysis was: glycine, 0; alanine, 0·97; valine, 0·34; leucine, 7·82; proline, 5·25; phenylalanine, 5·27; aspartic acid, 3·97; glutamic acid, 16·89; serine, 0; oxyproline, 0; tyrosine, 2·26; cystine, not determined; arginine, 7·2; histidine, 3·08; lysine, 4·28; ammonia, 2·32; tryptophan, present; total, 59·65%. W. D. H.

Constitution of Nucleo-proteins. The Constituents of Pepsin. Louis Hugounenq and Albert Morel (*Compt. rend.*, 1908, **147**, 212—214).—Crude pepsin extracted from the gastric mucous membrane of the pig by 4 parts of 0·2% hydrochloric acid at 50° yielded on hydrolysis by concentrated acids: tyrosine, 1·7%; alanine, 3·2%; valine, 7·5%; leucine, 11·4%; phenylalanine, 2·2%; lysine, 6·5%; arginine, 2·0%; adenine, 0·5%; xanthine, less than 0·01%; guanine, 0·2%; glucosamine, 1·4%; ψ-histidine, 0·4%, and ψ-lysines, 0·5%. The last-named substances are new; *ψ-histidine*, $C_4H_8O_2N_2$, is a diamino-acid, precipitable by silver nitrate, which was analysed as such and as the benzoyl derivative; the *ψ-lysines* are two substances yielding picrates which remain dissolved in the mother liquor of lysine picrate. One of the new picrates melts at 216°, and belongs to a substance, $C_{11}H_{24}O_5N_3$, which appears to be a dipeptide derived from lysine and glutamic acid. G. B.

Identity of Nucleic Acids of Thymus, Spleen, and Pancreas. Walter Jones (*J. Biol. Chem.*, 1908, **5**, 1—26).—It is pointed out that many of the differences which have been described in various nucleic acids are due to the difficulties in estimating their cleavage products, to different methods employed, and to admixture with guanylic acids. The three nucleic acids investigated in this research appear to be identical, the special points worked out being specific rotation under varying conditions, and the degree of viscosity of the sodium salts. The so-called gelatinous sodium salt and the non-gelatinous salt are readily convertible one into the other, and this offers a simple explanation of the physiological localisation and migration of nucleic acid. W. D. H.

Adsorption of Ferments. Leonor Michaelis (*Biochem. Zeitsch.*, 1908, **12**, 26—27. Compare this vol., i, 587).—By using more dilute solutions of pepsin, it is found that it is adsorbed by kaolin in acid or alkaline media. It is uncertain how much of this may not be due to mechanical adsorption. W. D. H.

Enzyme Action. XII. The Enzymes of Emulsin. Henry E. Armstrong, E. Frankland Armstrong, and Edward Horton (*Proc. Roy. Soc.*, 1908, **80**, *B*, 321—331).—The enzyme solutions were prepared for the purposes of the experiments directly from almonds. The extract at 15° exerted but little action on lactose, whereas β-methylglucoside underwent hydrolysis to a considerable extent; at 36° both substances were hydrolysed rapidly. On heating the extract at 45° for three hours, it lost its power of hydrolysing milk-sugar; it retained its activity as a hydrolyst of β-methylglucoside, amygdalin, and salicin, not only after twenty hours' heating at 45°, but also when heated for several hours at 55°. The enzyme was destroyed at about 59°. Other experiments were carried out with the object of effecting a separation of different enzymes by macerating almonds at different temperatures; by macerating with water at 0°, for example, and then macerating the extracted paste with a further quantity of water at 45°, two preparations of emulsins were obtained; both hydrolysed lactose at 38°; only that made at the lower temperature, however, produced any preceptible hydrolysis at 15°, indicating that the gluco-lactase had been preferentially extracted at 15°. The rate of hydrolysis of milk-sugar by extracts of almonds was investigated both without addition of, and in the presence of, added dextrose and galactose. The former alone caused considerable inhibition. The evidence obtained indicates the existence of a lactase in almonds, distinct from emulsin proper (β-glucase). Investigations were also made on the rate of hydrolysis of amygdalin, both the hydrocyanic acid and dextrose being estimated during the course of hydrolysis by special methods, which are described. The amount of Fischer's glucoside separated from partly hydrolysed material was always small; apparently there is no great difference in the rate at which this glucoside and amygdalin are hydrolysed by the β-glucase. S. B. S.

Action of Acids on the Coagulation of Milk by Vegetable Rennets. C. Gerber (*Compt. rend.*, 1908, **146**, 1111—1114).—It is shown that with vegetable ferments which coagulate boiled milk more readily than fresh milk, the addition of small quantities of citric, succinic, butyric, phosphoric, or hydrochloric acids retards the action of the rennet, whilst larger quantities accelerate it. In the case of rennets which curdle fresh milk more quickly than boiled milk, all the above acids, with the exception of citric acid, have an accelerating action; citric acid has a retarding effect, except when present in small quantity (compare Abstr., 1907, i, 1100). W. P. S.

Influence of Certain Iron Compounds and of Peroxydases on the Catalysis of Hydriodic Acid by Hydrogen Peroxide. JULES WOLFF and E. DE STOEKLIN (*Compt. rend.*, 1908, **146**, 1415—1417. Compare this vol., i, 490; ii, 573).—Colloidal ferrous ferrocyanide behaves as a peroxydase in most cases, but does not activate the decomposition of hydriodic acid by hydrogen peroxide. The latter activation is, however, brought about by ferric thiocyanate and by most peroxydases, but in the case of the ferments it appears to be due to the admixture of a specific enzyme, since particularly pure and potent peroxydases have been prepared which had but a feeble effect on the reaction between hydriodic acid and hydrogen peroxide.

G. B.

A Graphic Method for Registering Certain Fermentation Processes. CARLO FOÀ (*Biochem. Zeitsch.*, 1908, **11**, 382—399).—An apparatus is described for graphically registering oxidative processes taking place in the presence of oxydases. The substances under investigation are placed in one vessel, which is connected with a second vessel containing water, with a layer of oil on the surface to prevent oxidation. The two vessels are immersed in a constant-temperature bath, and can be filled with either air or oxygen. The second flask is connected with a Mosso plethysmograph. The apparatus is so arranged that, as the oxygen is used up in the process, water flows back from the plethysmograph into the second vessel; the amount which flows back can be automatically registered by means of a feather pointer on a blackened surface. A special thermo-regulator was constructed for maintaining constant temperatures, as the Ostwald thermostat was not sufficiently sensitive. The carbon dioxide evolved during the oxidative processes was also investigated. S. B. S.

Purification of Peroxydase. ALEXIS BACH and JACOB TSCHERNIACK (*Ber.*, 1908, **41**, 2345—2349).—Peroxydase, prepared by the Bach-Chodat method (Abstr., 1903, i, 377), always contains large amounts of carbohydrates and gum-like substances, and activates comparatively small amounts of hydrogen peroxide. Attempts to purify the peroxydase by alternate solution in water and precipitation by means of alcohol have been unsuccessful (this vol., i, 238). A more active peroxydase has now been obtained by treating the expressed juice of turnips with basic lead acetate, removing the excess of lead by means of sodium carbonate, dialysing the solution through a parchment membrane, and finally precipitating the peroxydase by means of alcohol. The peroxydase thus obtained forms a greyish-white powder, contains 7·87% of water, 81·66% of organic matter, 1·47% of ash, and 3·44% of nitrogen calculated for the ash-free substance, and has the activation coefficient, 22·7. As Stocklin's purified peroxydase, containing 11·41% water, 65·88% organic matter, 22·71% ash, and 3·43% nitrogen, had the activation coefficient 2, the activity of the peroxydase is evidently not related to its percentage of nitrogen or of ash. The new peroxydase gives the biuret and xanthoprotein reactions, but not Millon's reaction, and when heated evolves pyrrole and a strongly alkaline base. It renders hydrogen peroxide active towards the oxidation of phenols and aromatic bases, as also towards that of hydrogen iodide. These observations are in agreement with Bach's view (Abstr., 1907, i, 268, 810) that peroxydase is a single enzyme. Whilst when heated in the water-bath the purified peroxydase is destroyed completely only in eighteen minutes, if diluted with 20 vols. of water, it is destroyed under the same conditions in three minutes. G. Y.

Occurrence of Formaldehyde in Cell-free Fermentation. ALEXANDER LEBEDEFF (*Biochem. Zeitsch.*, 1908, **10**, 454—457).—In cases of fermentation by yeast juice in Walton's shaking apparatus, after the fermentation was over, and shaking was continued day and night, a reverse action occurred, and some of the carbon dioxide was absorbed. No proof, however, could be obtained that sugar was formed anew, but formaldehyde was found. W. D. H.

Preparation of Derivatives of *p*-Aminophenylarsinic Acid. KURATORIUM DER GEORG and FRANJISKA SPEYER'SCHEN STUDIENSTIFTUNG (D.R.-P. 193542).—*p*-Aminophenylarsinic acid condenses readily with aldehydes to furnish azomethine derivatives.

p-*Hydroxybenzylidene*-p-*aminophenylarsinic acid*,

$$OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_4\cdot AsO(OH)_2,$$

obtained by melting its components together at 140—150° and crystallising the product from alcohol, is a sparingly soluble, yellow powder, which is hydrolysed by boiling water, the components again condensing as the aqueous solution is cooled. Similar products are described from *p*-dimethylaminobenzaldehyde and resorcylaldehyde. G. T. M.

Secondary Aromatic Arsinic Acids. LOUIS BENDA (*Ber.*, 1908, **41**, 2367—2373).—Michaelis prepared dinitrodiphenylarsinic acid (Abstr., 1902, i, 515) from diphenylchloroarsine, but was unable to obtain the corresponding diamino-acid by reduction. Such diaminodiarylarsinic acids, $As(R\cdot NH_2)_2O\cdot OH$, have now been prepared by heating aromatic amines with arsenic acid at 170—180° (compare Bechamp, *Compt. rend.*, 1863, **56**, 1172). These diamino-acids resemble aminophenylarsinic acid in their general behaviour, having both acid and basic properties, but do not form precipitates with magnesia mixture, are soluble in alcoholic sodium hydroxide, and, when diazotised and coupled with β-naphthylamine, form dyes which are insoluble in alkalis. Unmordanted vegetable fibres have only a small affinity for the *dye* formed by coupling diazotised di-*p*-aminodiphenylarsinic acid with 6-amino-1-naphthol-3-sulphonic acid. When diazotised and boiled, the diaminodiarylarsinic acids yield the corresponding dihydroxy-acids, $As(R\cdot OH)_2O\cdot OH$.

Di-p-*aminodiphenylarsinic acid*, $C_{12}H_{13}O_2N_2As$, formed together with *p*-aminophenylarsinic acid by heating arsenic acid with aniline at 180—200°, crystallises in needles, m. p. 232°, and forms a white *precipitate* with silver nitrate in neutral solution. The *diacetyl* derivative, $C_{16}H_{17}O_4N_2As$, forms amber-coloured prisms, m. p. 263°. *Di*-p-*hydroxydiphenylarsinic acid*, $C_{12}H_{11}O_4As$, crystallises in plates, m. p. 239°.

Di-p-*aminodi*-o-*tolylarsinic acid*, $C_{14}H_{17}O_2N_2As$, crystallises in prisms, m. p. 243°. The *diacetyl* derivative, $C_{18}H_{21}O_4N_2As$, forms glistening prisms, m. p. 237°, decomp. 255°. *Di-p-hydroxy-o-tolylarsinic acid*, $C_{14}H_{15}O_4As$, has m. p. 247°. G. Y.

Magnesio-acetylene Bromide. II. BERNARDO ODDO (*Gazzetta*, 1908, **38**, i, 625—635. Compare Abstr., 1904, i, 862).—When magnesio-acetylene bromide is treated successively with carbon dioxide and dilute sulphuric acid, a small amount of propiolic acid is formed, the reactions being expressed by the equations:

$$CH⋮C{\cdot}MgBr + CO_2 = CH⋮C{\cdot}CO{\cdot}O{\cdot}MgBr$$

and $2CH⋮C{\cdot}CO{\cdot}O{\cdot}MgBr + H_2O + H_2SO_4 = MgSO_4 + MgBr_2 + H_2O + 2CH⋮C{\cdot}CO_2H$. The interaction of magnesio-acetylene bromide and water gives acetylene in small yield:

$$CH⋮C{\cdot}MgBr + H_2O = C_2H_2 + MgBr{\cdot}OH.$$

The hydrocarbon, m. p. 213—214°, which is obtained by the action of benzaldehyde on magnesio-acetylene bromide, to which the formula $C_{18}H_{14}$ was ascribed (*loc. cit.*), is shown to be *s*-tetraphenylethane, m. p. 209°. The formation of this compound and of the others mentioned (*loc. cit.*) is due to the interaction of benzaldehyde and magnesium phenyl bromide which has remained unchanged during the action of the acetylene. Phenylacetylenecarbinol is formed in small quantity by the action of benzaldehyde on magnesio-acetylene bromide and subsequent treatment with water:

$$Ph{\cdot}CHO + CH⋮C{\cdot}MgBr = MgBr{\cdot}O{\cdot}CHPh{\cdot}C⋮CH,$$

which with H_2O gives $OH{\cdot}CHPh{\cdot}C⋮CH$. T. H. P.

Organic Chemistry.

Formal Types of Structural Isomerides. CONRAD LAAR (*J. pr. Chem.*, 1908, [ii], **78**, 165—200).—An attempt to classify the different types of structural isomerides.

The main groupings are:

(I). Didesmic forms or isomerides with two changes of linking, for instance, $CH_3{\cdot}CHBr{\cdot}CH_3$ and $CH_3{\cdot}CH_2{\cdot}CH_2Br$.

(II). Tridesmic forms or isomerides with three changes of linking, such as *o*-nitrophenol and *o*-quinoneoxime.

(III). Tetradesmic forms or isomerides with four changes of linking, for instance, *p*-nitrosophenol and *p*-quinoneoxime.

Each of these main groups is divided into sub-groups: (*a*) Isomerism without change of valency; (*b*) isomerism with change of valency, and each sub-group is split up into a number of smaller divisions.

J. J. S.

Some Physical Properties of Butane and *iso*Butane. PAUL LEBEAU (*Bull. Acad. roy. Belg.*, 1908, 300—304).—The author has re-determined the boiling points and some other physical constants of butane and *iso*butane on specimens of the pure hydrocarbons obtained by the action of metalammonium compounds on the corresponding alkyl halide (Abstr., 1905, i, 401).

n-Butane, prepared by the action of sodammonium on *n*- or *sec.*-butyl iodide, solidifies in liquid air, has b. p. 0·5°/755 mm., and a critical temperature 151—152°; *iso*butane, obtained by the action of sodammonium or calcium-ammonium on *iso*butyl chloride, is also solid in liquid air, has b. p. −10·5°/757 mm. [Noyes, this vol., i, 305, finds b. p. −11·5°/760 mm.], and a critical temperature 134—135°. The solubilities of the two hydrocarbons in various solvents have also been determined, and the results are comprised in the following table:

	Pressure in millimetres of mercury.	Temperature.	Volume of gas dissolved in one volume of solvent.	
			Butane.	*iso*Butane.
Water	772	17°	0·15	0·13
Alcohol	775	17	18·83	13·2
Ether	773	18	29·8	27·9
Chloroform	768	17	32·5	39·5

M. A. W.

Molecular Weight of Hexacontane. KARL STRUVE (*Annalen*, 1908, **362**, 123—124).—Hexacontane was prepared by Hell and Hägele (Abstr., 1889, 575) by acting on myricyl iodide with potassium. These authors did not, however, determine the mol. wt. of the compound, and, since it might possibly be an unsaturated hydrocarbon,

$C_{30}H_{60}$, the mol. wt. has been determined by Landsberger's boiling-point method. The values obtained agree with the formula $C_{60}H_{122}$.

W. H. G.

Reciprocal Transformation of Isomerides under the Influence of Chemical Induction. SEBASTIAN M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 806—810).—It was discovered by Skraup (Abstr., 1891, 1338) that one exothermic reaction may induce another reaction, also exothermic, a phenomenon to which this author gave the name consonance. Thus, when hydrogen sulphide and sulphur dioxide react together in a medium containing maleic acid, the latter is transformed into fumaric acid.

The author gives further instances of this phenomenon. The transformation of *cyclo*propane into propylene is induced by the reaction $2NO + O_2 = N_2O_4$ at the ordinary temperature, but the interaction of hydrogen sulphide and sulphur dioxide has no such effect; so that not all exothermic reactions are able to induce isomeric change, the conditions necessary in any particular case being unknown.

T. H. P.

Action of Sulphur on Acetylene. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1908, 305).—Two years ago the author observed that thiophen is not formed by the action of acetylene on fused sulphur in the absence of air, and he is therefore able to confirm the results obtained by Capelle (this vol., i, 201).

M. A. W.

Preparation of Acetylene Di- and Tetra-chlorides from Acetylene and Antimony Pentachloride. HARRY K. TOMPKINS (D.R.-P. 196324).—Acetylene di- and tetra-chlorides (*s*-dichloroethylene and *s*-tetrachloroethane) may be prepared by passing the required amounts of acetylene into antimony pentachloride, or a mixture of this chloride with antimony trichloride, and then distilling the product, which contains probably an additive compound of acetylene and the pentachloride.

G. T. M.

Decomposition of Chloroform by Alcoholic Alkali Hydroxides. GUSTAV MOSSLER (*Monatsh.*, 1908, **29**, 573—581).—The decomposition of chloroform by alcoholic potassium hydroxide yields carbon monoxide, formic acid, and ethylene, the latter hitherto undetected. Contrary to the general belief, carbon monoxide is the main product; only in favourable circumstances is as much as half of the chloroform converted into formic acid. In the first two series of experiments, 20%, 5%, and 1% solutions of potassium hydroxide in absolute or in 50% alcohol are added to known amounts of chloroform. In all cases a constant volume ratio, 75 : 25, exists between the amounts of carbon monoxide and ethylene. The same ratio is attained in the third series of experiments, in which an alcohol-chloroform mixture is dropped on to powdered potassium hydroxide, provided that the molecular proportion of alcohol to chloroform exceeds 5 : 1.

The decomposition of chloral by alcoholic potassium hydroxide also leads to the formation of carbon monoxide and ethylene in the ratio 3 : 1 by volume.

The formation of these two gases is explained by the decomposition of the chloroform into hydrogen chloride and carbon dichloride, CCl_2, the transitory existence of which is indicated by the formation of carbonyl chloride in an experiment in which air and chloroform vapour are passed over a layer of potassium hydroxide. The production of formic acid is due to direct hydrolysis of the chloroform.

The decomposition of bromoform by alcoholic potassium hydroxide, in which, apart from potassium bromide, only carbon monoxide and ethylene in the ratio 3 : 1 are produced, is similarly explained by the total conversion of the bromoform into hydrogen bromide and carbon dibromide. The constant ratio of carbon monoxide to ethylene is explained by the action of the carbon dichloride on the alcohol, whereby the esters $CCl(OEt)$ and $C(OEt)_2$ are formed in the proportion of 1 : 2; the latter is directly hydrolysed, and the former decomposes into carbon monoxide and ethyl chloride, which is then converted by the alkali into ethylene. C. S.

Decomposition of Trichloro*iso*propyl Alcohol by Aqueous or Alcoholic Alkali Hydroxides. GUSTAV MOSSLER (*Monatsh.*, 1908, 29, 583—590. Compare preceding abstract).—The organic products of the decomposition of *ααα*-trichloro*iso*propyl alcohol by 5—20% aqueous potassium hydroxide are mainly carbon monoxide and acetaldehyde, together with small amounts of formic and lactic acids.

When 5% alcoholic potassium hydroxide (6 mols.) reacts with the alcohol (1 mol.), the chief products are acetaldehyde and formic acid, lactic acid being formed only in small amount; no gas is evolved unless the mixture is warmed, when a relatively small amount of carbon monoxide is liberated.

In no case could the intermediate formation of chloroform be detected.

The author's explanation is indicated in the scheme:

$$CH_3\cdot CH(OH)\cdot CCl_3 \longrightarrow HCl + CH_3\cdot C(OH)\colon CCl_2 \longrightarrow$$

$$CH_3\cdot C(OH)\colon CO \begin{array}{l} \xrightarrow{H_2O} CH_3\cdot CHO + CO \\ \\ \xrightarrow[EtOH]{} CH_3\cdot CHO + H\cdot CO_2H \end{array},$$

with the intermediate formation of ethyl formate.

C. S.

Composition of the Vapour from Mixtures of Ethyl Alcohol and Water. H. MASING (*Chem. Zeit.*, 1908, 32, 745).—With the object of verifying Gröhning's tables, a careful study of the composition of the alcohol vapour has been made, and it is found that the original values given by him are all too high; those given by Sorel are too low. The influence of pressure and the presence of impurities such as acetaldehyde, ethyl acetate, and amyl alcohol on the volatility has also been observed. J. V. E.

Preparation of Difluoroethyl Alcohol. Frédéric Swarts (*Bull. Acad. roy. Belg.*, 1908, 272—282).—In earlier papers (Abstr., 1903, i, 222, 725) the author has described the preparation of difluoroethyl alcohol by the action of metallic oxides and water on difluoroethyl bromide, and has shown that the best results are obtained with mercuric or lead oxide at 160°, but in no case is a theoretical yield obtained.

A repetition of the experiments, using large quantities (1400 grams) of difluoroethyl bromide, shows that when mercuric oxide is the hydrolytic agent, the yield of the alcohol is 93% of that required by theory, the 7% loss being due to a secondary reaction, yielding difluoroacetic acid (Abstr., 1903, i, 727) and mercurous bromide. When lead oxide replaces mercuric oxide, the yield of the alcohol amounts to 92% of that required by theory, the loss being again due to secondary reactions resulting in the formation of glycollic and oxalic acids, together with metallic lead. In this case, the lead oxide first hydrolyses the difluoroethyl alcohol to glycollaldehyde, which in its turn reduces the lead oxide, forming glycollic acid and metallic lead, and part of the glycollic acid undergoes a further oxidation, yielding oxalic acid.

M. A. W.

Methylation in the Ethylene Derivatives from the Point of View of Volatility. Louis Henry (*Compt. rend.*, 1908, **147**, 405—408).—The normal effect of the replacement of hydrogen combined with carbon in organic compounds by the methyl group is to raise the boiling point. This is the case even with the monatomic aliphatic alcohols. Substitution of hydrogen by methyl in the glycols, however, has the reverse effect, thus: $OH\cdot CH_2\cdot CH_2\cdot OH$ has b. p. 197—198°; $OH\cdot CHMe\cdot CH_2\cdot OH$, b. p. 188°; $OH\cdot CHMe\cdot CHMe\cdot OH$, b. p. 184°; $OH\cdot CMe_2\cdot CH_2\cdot OH$, b. p. 178°; $OH\cdot CMe_2\cdot CHMe\cdot OH$, b. p. 178°, and $OH\cdot CMe_2\cdot CMe_2\cdot OH$, b. p. 174°, although in the case of the corresponding hydrocarbons the b. p. rises regularly, thus: $CH_2{:}CH_2$, b. p. $-102°$; $CHMe{:}CH_2$, b. p. $-50°$; $CMe_2{:}CH_2$, b. p. $-6°$; $CHMe{:}CHMe$, b. p. 1—2°; $CMe_2{:}CHMe$, b. p. 36°; $CMe_2{:}CMe_2$, b. p. 72°. The explanation of this difference lies in the fact that the hydrocarbons are unimolecular, whilst their hydroxyl derivatives are associated in the liquid state.

The decreasing rise in boiling point as the hydrogen of methyl alcohol is replaced by methyl shows that the degree of association is thereby lowered, the elevation of the boiling point by increase in molecular weight being more and more counteracted by the decrease in molecular complexity. The progressive fall in the boiling points of the glycols indicates that here the latter effect is greater than the former.

The dichlorohydrins and the ethylene oxides derived from the above hydrocarbons correspond with the latter in volatility; thus the compounds resulting when the double linking in the above five hydrocarbons is saturated by chlorine (2 atoms) or by oxygen (1 atom) have their boiling points in the same order as those of the parent compounds. It is deduced that the oxides, as well as the chlorohydrins, are unimolecular or very slightly associated. E. H.

Use of Magnesium in place of Zinc in the Synthesis of Alcohols of the Allyl Series. W. JAVORSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 782—787).—Several authors have attempted to replace by magnesium the zinc employed in the synthesis of alcohols of the allyl series from an allyl haloid and a carbonyl compound, but with unsatisfactory results. The author finds, however, that this synthesis takes place readily if the reacting compounds in molecular proportions are allowed to act on magnesium (1 atom) in anhydrous ether. In this way, he has obtained good yields of (1) dimethylallylcarbinol from a mixture of allyl chloride and bromide with acetone; (2) phenylmethylallylcarbinol from allyl iodide or bromide and acetophenone; (3) diphenylallylcarbinol from allyl bromide and benzophenone; (4) methylpropylallylcarbinol from allyl bromide and methyl propyl ketone.

Also, ω-bromostyrene reacts readily in ethereal solution with magnesium, yielding styrene and diphenylvinylethylene. If the magnesium compound formed is treated with carbon dioxide, cinnamic acid, as well as diphenylvinylethylene, is formed. The reaction between magnesium and ω-bromostyrene hence proceeds in two directions: (1) the removal of the halogen from 2 molecules of the bromostyrene by the magnesium; (2) normally, giving an organo-magnesium compound, which, on decomposition with water, yields styrene and with carbon dioxide gives cinnamic acid. T. H. P.

Contact Oxidation of Ethyl Ether. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 799—800).—When oxidised by the contact process, ethyl ether yields acetaldehyde and a small proportion of formaldehyde: $Et_2O + O_2 = 2C_2H_4O + H_2O$; $Et_2O = 2C_2H_4 + H_2O$; $C_2H_4 + O_2 = 2CH_2O$. The gaseous products consist of carbon dioxide (7·55%), oxygen (2·11%), carbon monoxide (5·33%), hydrogen (1·86%), nitrogen (78·25%), and ethylene (2·9%). T. H. P.

Pressure and Composition of the Vapours of Aqueous Solutions of the Ether of Ethylene Glycol. A. E. MAKOVETZKI (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 752—760).—The author makes use of the following dynamical method, which allows of the simultaneous and accurate determination of the pressure and composition of the vapour from a mixture of two volatile liquids.

In a small thermostat filled with water at the room temperature is a flask containing air and provided with a manometer. By means of a known weight of water, a known volume of air, V, at pressure p mm., and saturated with water vapour having the pressure h at $t°$, is driven out of the flask, through a calcium chloride tube, and then through a nine-bulbed Will and Bredig apparatus placed in a thermostat and containing the solution to be investigated; in all the author's experiments, this second thermostat was maintained at 50 ± 0·05°. The vapour-laden air then passes through a spiral condenser immersed in solid carbon dioxide, and deposits its vapour quantitatively. The spiral is subsequently dipped into alcohol and into ether to remove traces of oil and water, and is then weighed, the increase in weight giving the amount of vapour in the volume V of air.

For determining the proportions of the ether of ethylene glycol and water in the condensed liquid, the author made use of the refractive index, which had been previously measured for a number of aqueous solutions of the ether.

Knowing the composition of the vapour, the number of milligram-mols. of each of the components in a weighed quantity of the condensed liquid can be calculated, and from the sum, a, of the numbers of milligram-mols. for the two components, the vapour pressure of the solution in mm. of mercury can be found by means of the equation: $H = B/[V(B+p-h)/22{\cdot}4.a.760(1+\alpha t)+1]$, where B is the atmospheric pressure, t the temperature of the thermostat containing the flask filled with air, and H the sum of the partial pressures of the two components of the vapour.

A solution containing 56·5 mols. % of the ether of ethylene glycol has the maximum vapour pressure, and boils unchanged. The specific heat and D of this solution are considerably higher than the calculated values.

For the pure ether, the mean specific heat at 16—100° is 0·4365—0·4377, and the heat of evaporation at atmospheric pressure, 89·95—90·08 Cals. per gram. Trouton's constant is hence 21·2, which shows that in the liquid condition the ether is not associated, although the lowering of the partial pressure of water by the vapour is twice as small as it should be according to Raoult's law. T. H. P.

Studies in Steam Distillation. Formic and Acetic Acids. H. Droop Richmond (*Analyst*, 1908, **33**, 305—312).—The results of experiments on the rate of distillation of aqueous solutions of formic and acetic acids are given, the apparatus employed being specially designed to prevent condensation in the head of the retort. The rate of distillation of the acids relatively to that of water is given, together with the results calculated from the formulæ given previously (this vol., i, 495). W. P. S.

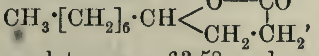
Spectroscopic Reaction for Oleic Acid. Isaac Lifschütz (*Zeitsch. physiol. Chem.*, 1908, **56**, 446—452).—The characteristic reaction given by oleic acid (this vol., i, 263) is best shown when an acetic acid solution of chromic acid is used as the oxidising agent. To a mixture of 1 drop of oleic acid in 3—4 c.c. of glacial acetic acid and 1 drop of a 10% solution of chromic acid, also in glacial acetic acid, 10 drops of concentrated sulphuric acid are added. After a short time, a violet to cherry-red coloration develops, and ultimately becomes so deep that dilution with acetic acid is necessary before the characteristic absorption bands can be observed. Oleoglycerides give the same reaction, but the addition of chloroform is advisable.

The sensitiveness is 1 in 10,000 to 1 in 15,000.

Trichloroacetic acid produces the same coloration as the acetic and sulphuric acids. These reactions for oleic acid and cholesterol are thus practically identical. J. J. S.

Formation of γ-Lactones. Alexis A. Shukoff and Peter J. Schestakoff (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 830—839).—The authors have investigated the conditions of transformation of oleic acid into lactone, and also the extent to which other unsaturated ethylenic acids with the double linking not in the γ-position are able to undergo this transformation. It has been found that saturated alcohol-acids also yield lactones, the hydroxyl group wandering to the γ-position, giving a γ-hydroxy-acid and subsequently a γ-lactone. The best method of converting the acids into lactones is to heat them with anhydrous zinc chloride or concentrated sulphuric acid. When treated in this way, oleic, elaidic, *iso*oleic, θ-hydroxystearic, and ι-hydroxystearic acids all yield γ-stearolactone, erucic acid yields γ-behenolactone, and κλ-undecylic acid, γ-undecolactone. Crotonic and α-hydroxybutyric acids, however, give no lactone. Indeed, under these conditions, lactones are only given by those ethylenic acids and saturated hydroxy-acids in which the double linking or hydroxyl group is at least four carbon atoms away from the carboxyl group.

It is probable that the oleic acid separated from fats is not a chemical individual, but consists of a mixture of isomerides having double linkings, not only in the θι-position, but also in the βγ- or γδ-position. To see whether it is the latter alone which yields lactone, the θι-acid was prepared from ι-hydroxystearic acid, and was found to give about 10% of γ-stearolactone when treated with zinc chloride. γ-Stearolactone, obtained in 35% yield by the action of concentrated sulphuric acid on commercial oleic acid (compare Abstr., 1904, i, 646), has an iodine number 16—20 and a mean molecular weight, assuming it to be a monobasic acid, 375, which, after boiling with alcoholic potassium hydroxide, falls to 291. This indicates that the lactone contains a considerable proportion of a compound with the character of an anhydride or complex ether, analogous to those formed on heating hydroxystearic acid. After distillation, the iodine number and, consequently, the proportion of unsaturated compound increase considerably, indicating the presence of hydroxystearic acids, which are converted into unsaturated acids on distillation. If the pure stearolactone is treated with sulphuric acid, it is partly converted into soluble, acid products, which contain sulphur and are probably sulphonic-acids. Conversion of part of the stearolactone into these sulpho-compounds probably determines, to some extent, the small yield of the lactone.

γ-Behenolactone,  $CH_3\cdot[CH_2]_6\cdot CH<\begin{matrix}O\text{—}CO\\ CH_2\cdot CH_2\end{matrix}$, crystallises from light petroleum in shining plates, m. p. 63·5°, and, on oxidation with chromic acid, yields *γ-ketobehenic acid*, $C_{22}H_{42}O_3$, forming colourless crystals, m. p. 103°.

γ-Undecolactone, $C_{11}H_{20}O_2$, b. p. 286°, is converted into γ-hydroxyundecoic acid, m. p. 34°, by acids or alkalis. T. H. P.

Complex Ozo-salts of Tungsten. Arrigo Mazzucchelli and Giuseppe Inghilleri (*Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 30—33. Compare Abstr., 1907, i, 748).—The tendency of tungsten to form ozo-salts is not so marked as that exhibited by its higher analogue, uranium, or by molybdenum, and the ozo-salts are readily soluble and difficult to obtain free from the normal salts used in their preparation. On this account no lithium ozotungsten oxalate could be isolated, whilst the potassium and barium salts were only obtained in an impure condition.

Sodium ozotungsten oxalate, $Na_2C_2O_4,WO_4,5H_2O$, obtained by the action of hydrogen peroxide on the compound $Na_2C_2O_4,WO_3$, forms white crystals. The corresponding *ammonium* salt,

$$(NH_4)_2C_2O_4,WO_4,H_2O,$$

forms white, sphaero-crystals; the *calcium* salt, CaC_2O_4,WO_4,H_2O, was also prepared. T. H. P.

Esterification of Malonic Acid. Isaac K. Phelps and E. W. Tillotson, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 243—252).—In earlier papers (Abstr., 1907, i, 823; this vol., i, 166), methods have been described for obtaining good yields of ethyl succinate and benzoate. A study has now been made of the best conditions for the esterification of malonic acid. The largest yield, 96·1%, was obtained by heating an alcoholic solution of malonic acid with sulphuric acid at 50° for eight hours, and treating the residue with a fresh quantity of alcohol for two hours. E. G.

Purification of Esters. Isaac K. Phelps, M. A. Phelps, and E. A. Eddy (*Amer. J. Sci.*, 1908, [iv], 26, 253—256).—A study has been made of the purification of ethyl succinate, malonate and benzoate, containing alcohol, water, unchanged organic acid, and small quantities of mineral acid. It has been found that these esters may be purified without much loss by heating them in suitable conditions with dry potassium carbonate under reduced pressure. A comparison of this method with that of extracting the ester with ether has shown that the loss by the former method is rather greater in the case of ethyl benzoate, but is smaller in the cases of ethyl succinate and malonate. The potassium carbonate method, however, is to be preferred even with ethyl benzoate, since it affords greater ease of manipulation and is less expensive. The smaller the quantity of free acid present, the more completely can the ester be recovered. E. G.

Conversion of Ethyl Cyanoacetate into Ethyl Malonate. Isaac K. Phelps and E. W. Tillotson, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 257—263).—The conditions under which ethyl cyanoacetate is converted into ethyl malonate have been carefully investigated. It was found that when a well-cooled mixture of 50 grams of ethyl cyanoacetate, 125 c.c. of absolute alcohol, and 4 grams of sulphuric acid was saturated with hydrogen chloride by passing in a stream of the dry gas for four hours, and the product heated for two hours at 100—110° with 200 c.c. of absolute alcohol, a yield of 96·3% of ethyl malonate was obtained. E. G.

Influence of Catalytic Agents in Ester Formation. Esterification of Cyanoacetic Acid. Isaac K. Phelps and E. W. Tillotson, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 264—266).—The effects produced on the esterification of cyanoacetic acid by varying the proportions of the reagents, the catalysers, and the time of reaction have been studied. The results show that by the use of alcohol alone, a yield of 63% of the ester can be obtained, but that the yield is increased by the presence of a catalytic agent, and within certain limits by the amount of the catalyst employed. The esterification is rendered more complete by increasing the time of reaction. Alcoholic hydrogen chloride causes the formation of some ethyl malonate, but this change does not occur when sulphuric acid is employed. Nearly theoretical yields of ethyl cyanoacetate can be obtained by heating 50 grams of cyanoacetic acid with 2 grams of sulphuric acid and 200 c.c. of absolute alcohol for two hours at 100—110°. E. G.

Preparation of Malonic Acid or its Ester from Monochloroacetic Acid. Isaac K. Phelps and E. W. Tillotson, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 267—274).—In earlier papers (preceding abstracts) an account has been given of the best conditions for the esterification of malonic acid and for the conversion of ethyl cyanoacetate into ethyl malonate. A further study has now been made with special reference to the preparation of ethyl malonate from chloroacetic acid.

It has been found that the reaction between potassium cyanide and sodium chloroacetate to form sodium cyanoacetate proceeds best in alkaline solution, and takes place vigorously at 110°, or slowly at 90—95°, without affecting the yield of ethyl malonate. The alkaline solution of sodium cyanoacetate should not be evaporated to dryness at a high temperature, or even be boiled for a long time, since these conditions favour the formation and subsequent decomposition of sodium malonate. After acidifying the solution of sodium cyanoacetate with sulphuric acid and removing the precipitated salt by filtration, the resulting solution of cyanoacetic acid is concentrated under reduced pressure at 70—80°. The precipitated salt is washed with alcohol, and the alcoholic solution is evaporated at about 60°. The residues, consisting of cyanoacetic acid and some of its ester and sodium salt, are converted into ethyl malonate by the method described previously (*loc. cit.*). By this means a yield of 92% of ethyl malonate can be obtained.

The ester can be converted into pure malonic acid by heating it with an equal quantity of water and a few drops of nitric acid at about 60° for some time after the mixture has become homogeneous, and evaporating the solution to the point of saturation. The malonic acid which separates on cooling is recrystallised from hot water. E. G.

Preparation of Cyanoacetic Acid and its Ester from Monochloroacetic Acid. Isaac K. Phelps and E. W. Tillotson, jun. (*Amer. J. Sci.*, 1908, [iv], 26, 275—280).—Sodium chloroacetate and potassium cyanide react quantitatively in alkaline solution to form sodium cyanoacetate. A study has now been made of the formation of ethyl cyanoacetate from monochloroacetic acid, the method of esterification of cyanoacetic acid being that described previously (preceding abstract). The results show that ethyl cyanoacetate can be obtained in good yield if precautions are taken to minimise the transformation into malonic acid. Pure cyanoacetic acid can be prepared by heating a mixture of two parts of water with one part of the ester and a few drops of nitric acid at about 60° for some time after the mixture has become homogeneous. The solution is then evaporated at 50–60° to the point of saturation, and the cyanoacetic acid which separates on cooling is recrystallised from a mixture of ether and chloroform.

E. G.

Saponification of Fats by means of Hydroxylamine. EUGENIO MORELLI (*Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 74—78).—In order to obtain derivatives of fats which crystallise well and have melting points higher than those of the acids from which they are derived, the author has studied the action of hydroxylamine on fats. The hydroxamic acids obtained are very stable, and fulfil the above conditions.

Stearohydroxamic acid, $C_{17}H_{35}\cdot C(OH)\colon NOH$, prepared from tristearin and hydroxylamine, separates from alcohol in crystals, m. p. 104°, and in alcoholic solution gives a reddish-violet colour with ferric chloride.

Palmitohydroxamic acid, $C_{15}H_{31}\cdot C(OH)\colon NOH$, which is deposited from alcohol in crystals, m. p. 99°, and *oleohydroxamic acid*,

$$C_{17}H_{33}\cdot C(OH)\colon NOH,$$

m. p. 61°, both give the red colour with ferric chloride in alcoholic solution. The latter is resolved into oleic acid and hydroxylamine sulphate when boiled with dilute sulphuric acid.

A mixture of stearohydroxamic and palmitohydroxamic acids has m. p. 95°; the lowering of m. p. here observed can doubtless serve to establish the proportions of the two acids in a mixture of them.

T. H. P.

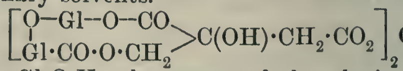
New Synthesis of Citric Acid. ENOS FERRARIO (*Gazzetta*, 1908, **38**, ii, 99—100).—By the condensation of ethyl bromoacetate with diethyl oxalate in presence of magnesium according to the equation:

$$CO_2Et\cdot CO_2Et + 2CH_2Br\cdot CO_2Et + 2Mg = Br\cdot Mg\cdot OEt + CO_2Et\cdot CH_2\cdot C(OMgBr)(CO_2Et)\cdot CH_2\cdot CO_2Et,$$

the author obtains a compound which, when treated with dilute sulphuric acid, yields an oil, b. p. 215°/35 mm., and appears to be triethyl citrate. The reaction is being studied further. T. H. P.

Structure of Glucinum Salts. SEBASTIAN M. TANATAR and E. K. KUROVSKI (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 787—790. Compare Abstr., 1907, i, 888; this vol., i, 166, 502).—The following salts of glucinum have been prepared:

With tricarballylic acid, the *salt*, $Gl_3(C_6H_5O_6)_2$, obtained as a white powder insoluble in all the ordinary solvents.



With citric acid, the *salt*, $\left[\begin{array}{l}O-Gl-O-CO\\ \mid\\ Gl\cdot CO\cdot O\cdot CH_2\end{array}\!\!>C(OH)\cdot CH_2\cdot CO_2\right]_2Gl$, which is of a more basic type, $Gl_5O_2X_2$, than most of the glucinum salts, Gl_4OX_6.

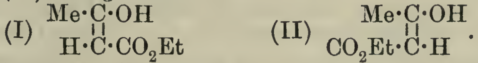
With salicylic acid, glucinum forms the *salt*, $(OH\cdot C_6H_4\cdot CO_2Gl\cdot O)_2Gl$;

with phthalic acid, the *salt*, $C_6H_4 \left< \begin{array}{l} CO_2Gl\cdot CO_2\cdot C_6H_4\cdot CO_2Gl\cdot O \\ CO_2Gl\cdot CO_2\cdot C_6H_4\cdot CO_2Gl\cdot O \end{array} \right> Gl$, and with lactic acid, the *salt*, $(OH\cdot CHMe\cdot CO_2Gl\cdot O)_2Gl$.

In addition to the benzoate already described (this vol., i, 166), glucinum yields a *benzoate* of the normal type, $Gl_4O(C_7H_5O_2)_6$, which is obtained on prolonged boiling of a solution of benzoic acid in a mixture of equal volumes of alcohol and benzene with glucinum carbonate; this salt has the molecular weight 710 (theor. 779) in freezing benzene.

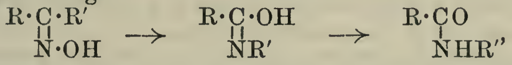
The interaction of sodium benzoate and a glucinum salt in aqueous solution yields various salts, which are more or less basic according to the concentrations, temperatures, and acidities of the solutions, and are insoluble in organic solvents. T. H. P.

Isomerism of Ethyl Acetoacetate. R. H. McCrea (*Chem. News*, 1908, 98, 127).—The enolic form of ethyl acetoacetate may, like other unsaturated compounds, be represented as having a *trans*- (I) and a *cis*- (II) configuration:



$$\text{(I)}\ \begin{array}{l} Me\cdot C\cdot OH \\ \quad \| \\ H\cdot C\cdot CO_2Et \end{array} \qquad \text{(II)}\ \begin{array}{r} Me\cdot C\cdot OH \\ \| \quad\quad \\ CO_2Et\cdot C\cdot H \end{array}.$$

The *cis*-configuration (II) must be unstable, as it corresponds with the hypothetical intermediate product in Bernthsen's representation of the Beckmann change:



$$\begin{array}{l} R\cdot C\cdot R' \\ \quad \| \\ \quad N\cdot OH \end{array} \longrightarrow \begin{array}{l} R\cdot C\cdot OH \\ \quad \| \\ \quad NR' \end{array} \longrightarrow \begin{array}{l} R\cdot CO \\ \quad | \\ \quad NHR'' \end{array}$$

and must therefore change at once into the ketonic form of the ester. The action of phosphorus pentachloride leads, now, to the formation of β-chlorocrotonic acid, $\begin{array}{l} Me\cdot C\cdot Cl \\ \quad \| \\ H\cdot C\cdot CO_2H \end{array}$ or $\begin{array}{r} Me\cdot C\cdot Cl \\ \| \quad\quad \\ CO_2H\cdot C\cdot H \end{array}$. This acid should be stable, as it cannot undergo the second stage of the Beckmann change; in agreement with this view is its conversion into *iso*crotonic acid, which is considered to be the stereoisomeride of crotonic acid. It cannot be decided which of the modifications, the stable or the unstable, has the *cis*-configuration, as either configuration might be the unstable form. It is suggested that *iso*crotonic acid has the form $\begin{array}{r} Me\cdot C\cdot OH \\ \| \quad\quad \\ CO_2H\cdot C\cdot H \end{array}$, as it is formed from the chloro-acid, which also forms tetrolic acid, $\begin{array}{r} Me\cdot C \\ \| \\ CO_2H\cdot C \end{array} + \begin{array}{c} Cl \\ | \\ H \end{array}$, and may therefore be considered to have the hydrogen and chlorine atoms spatially near each other, $\begin{array}{r} Me\cdot C\cdot Cl \\ \| \quad\quad \\ CO_2H\cdot C\cdot H \end{array}$. G. Y.

Action of Magnesium on Esters of Brominated Fatty Acids. New Synthesis of Ketonic Esters. Josef Zeltner (*J. pr. Chem.*, 1908, [ii], 78, 97—123. Compare this vol., i, 243).—In the ordinary Reformatzky synthesis of hydroxy-acids, the zinc cannot be replaced by magnesium. When magnesium is used, at least three reactions take place: (1) Reduction of the brominated ester to the corresponding fatty ester; (2) formation of a β-ketonic ester; (3) production of a high boiling, crystalline compound. The yield of ketonic ester is best when an *iso*bromo-ester is used, for example:

Ethyl bromopropionate	gives	35·3	per cent.	ethyl propionylpropionate.
Ethyl bromobutyrate	,,	40·5	,,	ethyl butyrylbutyrate.
Ethyl bromo*iso*butyrate	,,	67·3	,,	ethyl *iso*butyryldimethylacetoacetate.
Ethyl bromo*iso*valerate	,,	60·3	,,	ethyl valerylvalerate.

The difference in the reactions with zinc and magnesium is accounted for by the relative stabilities of the compounds

$$>\mathrm{CMgBr{\cdot}CO_2Et} \text{ and } >\mathrm{CZnBr{\cdot}CO_2Et}.$$

By the action of *p*-tolualdehyde on the product of the interaction of magnesium and ethyl α-bromo*iso*butyrate, a small amount of a crystalline substance, $C_{16}H_{20}O_3$, m.p. 138—139°, is obtained.

Ethyl iso*butyryldimethylacetate*, $\mathrm{CHMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et}$, has b. p. 202·5—203°/745·5 mm., and, when boiled with aqueous potassium hydroxide, yields di*iso*propyl ketone. It is formed from ethyl α-bromo*iso*butyrate by the following series of reactions:

$$\mathrm{2CMe_2(MgBr){\cdot}CO_2Et} \longrightarrow \mathrm{CMe_2(MgBr){\cdot}C(OEt)(OMgBr){\cdot}CMe_2{\cdot}CO_2Et}$$
$$\longrightarrow \mathrm{CHMe_2{\cdot}C(OEt)(OH){\cdot}CMe_2{\cdot}CO_2Et} \longrightarrow \mathrm{CHMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et}.$$

Ethyl butyrylbutyrate has b. p. 222·8—223·4°/755 mm. (compare Hamonet, Abstr., 1890, 235).

Ethyl iso*valeryl*iso*valerate*, $\mathrm{CHMe_2{\cdot}CH_2{\cdot}CO{\cdot}CH(CHMe_2){\cdot}CO_2Et}$, obtained from ethyl α-bromo*iso*valerate, has b. p. 237·2—237·4°/768 mm. (corr.), and, on hydrolysis, yields *iso*valerone.

Ethyl bromoacetate does not give ethyl acetoacetate (compare Stollé, this vol., i, 310). J. J. S.

Methyl Mesoxalate and Some of its Reactions. Richard S. Curtiss and Paul T. Tarnowski (*J. Amer. Chem. Soc.*, 1908, **30**, 1264—1271).—In an earlier paper (Curtiss, Abstr., 1906, i, 480), a method was described for the preparation of ethyl mesoxalate by the action of nitrogen trioxide on ethyl malonate by which a yield of 90—95% could be obtained.

It has now been found that a yield of 80—85% of methyl mesoxalate can be obtained in a similar manner. The mother liquor obtained in this reaction yields a light green mixture of unstable, oily esters, which are of an acid nature and contain nitrogen. This product decomposes suddenly at 120—130°, and yields yellow potassium, ammonium, and silver salts.

When methyl mesoxalate is distilled under reduced pressure, methyl oxomalonate, $\mathrm{CO(CO_2Me)_2}$, b. p. 100°(uncorr.)/20 mm., is obtained. Pure anhydrous methyl oxomalonate has been prepared, and its reactions are being studied.

By the action of hydrazine carbonate on methyl mesoxalate, a compound, probably *methyl hydrazotartronate*,

$$\mathrm{(CO_2Me)_2C(OH){\cdot}NH{\cdot}NH{\cdot}C(OH)(CO_2Me)_2},$$

m. p. 154—155°, is obtained, which forms white crystals. If this substance is mixed with phosphoric oxide, it is converted into a yellow, crystalline compound, which is probably an azimethylene derivative. When the hydrazo-compound is treated with benzaldehyde, benzylideneazine (Curtius and Jay, Abstr., 1889, 393) is produced. E. G.

Conversion of Methyl Alcohol into Formaldehyde and Preparation of Formalin. IV. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 796—799. Compare this vol., i, 77).—The author gives further details for carrying out this oxidation. Platinised pumice and platinised asbestos act as good catalysts. By using these, the preliminary heating in a furnace of the tubes containing copper gauze may be dispensed with. The proportion of acetone in the methyl alcohol should not exceed 2%. When 4% of acetone is present, the contact mass does not ignite, and with 2·5%, ignition takes place when the temperature is 34—35° and the current of air amounts to 3 litres per minute; only when the greater part of the acetone has burnt away does the copper gauze begin to ignite. T. H. P.

Condensation Products of Acetaldehyde containing Six and Ten Atoms of Carbon. SIMON ZEISEL and BÉLA VON BITTÓ (*Monatsh.*, 1908, **29**, 591—605).—Ten volumes of acetaldehyde are heated for thirty-six hours at 95—97° with 1 volume of saturated sodium acetate solution, and the product distilled in steam. The distillate is fractionated, and, after removal of crotonaldehyde, the portion boiling above 120°, purified by repeated distillation in steam, shaking with calcium carbonate, and drying, is separated by fractional distillation into two *substances*, both having the composition C_6H_8O and exhibiting the properties of an aldehyde with two ethylenic linkings; the one has b. p. 75—80°/24—26 mm., yields an impure *oxime*, m. p. 155·5°, and an unstable, crystalline phenylhydrazone, whilst the other has b. p. 55—60°/24—26 mm. and 141—143° under ordinary pressure, forms an unstable oxime and phenylhydrazone, and yields, by oxidation with free oxygen, formic acid and resinous and other unexamined products.

From the residue of the original preparation non-volatile in steam, a *substance*, $C_{10}H_{14}O_2$, b. p. 159—163°/16·5 mm., has been isolated, which contains one CHO group (the other oxygen atom being probably in the form of a "bridge"), does not form a definite oxime or phenylhydrazone, and reacts with bromine, evolving hydrogen bromide. C. S.

Crystalline Polymeride of *iso*Butaldol. R. MUSSELIUS (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 822—826).—The author has subjected to further investigation the crystalline substance, m. p. 90—92°, isolated by Brauchbar (Abstr., 1897, i, 137) from the condensation products of *iso*butaldehyde, and characterised by him as *iso*butaldol. By repeated fractional crystallisation from benzene, the compound is obtained in bundles of slender, white needles, m. p. 96·5—97°. In freezing benzene, the molecular weight corresponds with the formula $(C_8H_{16}O_2)_2$, a result in accordance with those of Kohn (Abstr., 1900, i, 274) for other crystalline aldols, which were all found to be bimolecular polymerides of the liquid aldols. In freezing acetic acid, the molecular weight is 300—309·5 (theory, 288), but ebullioscopic measurements in ether gave unsatisfactory results, probably owing to decomposition of the double molecules of the aldol. T. H. P.

Preparation of Ketone ortho-Ethers. Edgar Hess (D.R.-P. 197804).—Nitriles of the general formula R·CN are converted into the hydrochlorides of imino-esters by treatment with hydrogen chloride in absolute alcohol, and the product mixed with a ketone in the same medium. After eight days' shaking, the ammonium chloride produced is precipitated by ether, the filtrate poured into ice water, and the ketone ortho-ether separated from any ester by fractional distillation. The following acetals were thus produced: From methyl ethyl ketone, $CMeEt{\cdot}C(OEt)_2$, b. p. 68°/10 mm., 120°/760 mm.; from diethyl ketone, $CEt_2{\cdot}C(OEt)_2$, b. p. 71°/44 mm., 154°/760 mm., and from dipropyl ketone, $CPr_2{\cdot}C(OEt)_2$, b. p. 69°/12 mm. G. T. M.

Action of Ammonia on Methyl Ethyl Ketone. Carl Thomae (*Arch. Pharm.*, 1908, **246**, 373—377).—The use of alcohol as a solvent in this reaction, described by Traube (this vol., i, 362), was introduced by the author (Abstr., 1905, i, 509). G. B.

Solubility and Certain Reactions of Pinacolin. Léon Delange (*Bull. Soc. chim.*, 1908, [iv], **3**, 910—915).—The author finds that, contrary to Denigès' statement (Abstr., 1903, i, 606), pinacolin does not form an additive compound with mercuric sulphate, but that the precipitate obtained with ordinary samples of pinacolin is due to the presence of impurities which are not entirely removed by fractionation. In order to prepare pure pinacolin, the ordinary product is rectified seven times with a Le Bel column, warmed with mercuric sulphate, and the filtrate again warmed with the reagent. After decanting, the pinacolin is dried, washed, and rectified (b. p. 106·2°). Pure pinacolin dissolves in water to the extent of 2·44% at 15°, and its solubility at 15° in aqueous acetone is (by volume) 1 part in 28·8 parts of 20%, 1 in 16·5 of 33%, 1 in 11·0 of 50%, and 1 in 7·0 of 60%. When 1 c.c. of pinacolin is added to a mixture of 0·45 c.c. of acetone and 1·8 c.c. of water, 0·30 c.c. of acetone is absorbed by the water and 0·15 c.c. by the pinacolin, and in a mixture of 1·65 c.c. of acetone and 0·85 c.c. of water, 0·75 c.c. of acetone is absorbed by the water and 0·60 c.c. by the pinacolin. The author shows that acetone can be estimated in presence of pinacolin by precipitation with mercuric sulphate. Pure pinacolin gives Legal's colour reaction (Abstr., 1897, ii, 467), as stated by Denigès, but it does not furnish iodoform when treated with iodine and potassium hydroxide; the precipitate obtained is soluble in acetic acid, and has m. p. 68°, and at the same time there is formed a small amount of a volatile liquid of a piquant odour. J. C. C.

Action of Hydroxylamine on Ketones of the Type $CHR{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}R$.

Roberto Ciusa and A. Terni (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 724—728. Compare Abstr., 1907, i, 62).—In addition to the compounds α-cinnamylideneacetophenonehydroxylamine and α-cinnamylideneacetophenoneoxime previously isolated as products of the action of hydroxylamine on cinnamylideneacetophenone, isomeric forms of these substances can also be separated in small quantities. These are denoted as β-forms, and their properties are compared with those of the α-compounds.

α-Cinnamylideneacetophenoneoxime (m. p. 135°) gives a *benzoyl* derivative crystallising from alcohol in white needles, m. p. 125°. *β-Cinnamylideneacetophenoneoxime* crystallises in white needles, m. p. 139—140°, and gives a benzoyl derivative, m. p. 137°. *β-Cinnamylideneacetophenonehydroxylamine* forms small, white spangles, m. p. 196°.

Cinnamylideneacetophenone is not toxic in its properties; the α-oxime is more poisonous, but 4—5 grams can be administered per day; so-called resinoid acids are then found in the urine, together with large quantities of urorosein. The latter fact is remarkable, as uroroseinuria has not previously been induced by artificial means. α-Cinnamylideneacetophenonehydroxylamine differs from the other substances in being highly poisonous, probably in virtue of the ·NH·OH group, as in the case of phenylhydroxylamine. W. A. D.

N-Alkylketoximes. JOHANNES SCHEIBER (*Annalen*, 1908, **362**, 54—63).—Previous work has shown that *N*-alkylketoximes are produced only with great difficulty by the condensation of β-substituted hydroxylamines with ketones (compare Scheiber and Wolf, Abstr., 1907, i, 1028). In the case of acetone, ethyl acetoacetate, methyl ethyl ketone, and diacetyl, the additive compounds first formed by the reaction with the β-substituted hydroxylamine, namely, *N*-alkylketoxime hydrates, were isolated, but similar substances were not obtained from benzyl methyl diketone or benzil. With the object of ascertaining to what extent various ketones condense with β-benzylhydroxylamine, the following method was devised, by which the isolation of the additive product became unnecessary.

Known weights of β-hydroxylamine and of the ketone are added to a known weight of benzene, and the depression of the freezing point of the solvent noted at once and at intervals of some hours. If no interaction takes place, the depression observed is that calculated from the weights of ketone and β-benzylhydroxylamine added; should the observed depression be smaller than the calculated, then interaction must have taken place. Methyl ethyl diketone is found to react at once, whilst benzil does not react with β-benzylhydroxylamine.

The following ketones interact slowly with β-benzylhydroxylamine, the difference between the observed and calculated depression of the freezing point increasing slowly during several hours: acetone, methyl ethyl ketone, methyl propyl ketone, methyl *iso*propyl ketone, methyl butyl ketone, benzyl methyl ketone, diethyl ketone, acetophenone, and *m*-nitroacetophenone. It is found that the homologues of acetone do not condense so readily with β-benzylhydroxylamine as acetone itself, with the one exception of benzyl methyl ketone, which apparently interacts more rapidly than acetone. The additive power of the ketone is reduced considerably by replacing a methyl group by ethyl, phenyl, or *m*-nitrophenyl.

The effect on the rate of formation of the additive compounds, produced by the addition of *p*-toluidine, diphenylamine, dimethylaniline, triethylamine, and tribenzylamine, was also investigated.

Generally speaking, the presence of a base does not bring about an acceleration in the rate of condensation; in fact, triethylamine appears to retard the reaction. W. H. G.

***N*-Alkylketoximes.** JOHANNES SCHEIBER and PAUL BRANDT (*Annalen*, 1908, **362**, 64—77).—The work described in the previous paper (compare Scheiber, preceding abstract) has been repeated, and so that the reactivities of the various ketones might be compared, equal molecular solutions have been used in each case. In all cases an experiment was performed in which the molecular proportions of ketone and β-benzylhydroxylamine were as 1 : 1, and sometimes as 5 : 1. The results obtained may be summarised as follows:

(1) In the absence of a base, the rate of formation of the additive product decreases rapidly in the following order: benzyl methyl ketone, acetone, methyl butyl ketone (methyl ethyl ketone = methyl hexyl ketone), diethyl ketone, acetophenone. Acetophenone, even in strong solutions, is almost indifferent towards β-benzylhydroxylamine.

(2) In the presence of a base, such as triethylamine, tribenzylamine, or dimethylaniline, the rate at which the additive product is formed is apparently smaller, but it is only apparent, for in some cases the difference between the calculated and observed depression of the freezing point at first increases and then decreases, undoubtedly because the second reaction, *N*-benzylketoxime hydrate ⟶ *N*-benzylketoxime + water, is taking place. The apparent reduction in the velocity of formation of the *N*-benzylketoxime hydrate is due to the occurrence of this second reaction. In fact, the solution containing β-benzylhydroxylamine, benzyl methyl ketone, and triethylamine, or tribenzylamine, becomes turbid after some time, owing to separation of water.

It is therefore evident that the difference in the behaviour of an aldehyde and a ketone towards β-substituted hydroxylamines is merely one of degree and not of kind. W. H. G.

The Scission of Sugars. [Sucroclasm.] II. The Action of Zinc Dust and Iron on Formaldehyde Solutions; the Action of Zinc Dust on Dextrose. WALTHER LÖB (*Biochem. Zeitsch.*, 1908, 12, 466—472. Compare this vol., i, 715).—As products of the action of zinc dust on formaldehyde were isolated, formic acid and two other volatile products were obtained in the form of their condensation products with phenylhydrazine. The one gave an insoluble osazone, m. p. 243°, which corresponded in properties with diacetylosazone, and the other gave an osazone, m. p. 148°, which is methylglyoxalosazone. The other products of reaction have not yet been all identified. They appear to include β-acrose, as an osazone of m. p. 165° was obtained. Polyhydroxy-acids were also obtained. When formaldehyde solutions are treated with iron, condensation to sugars takes place to only a slight extent, and only traces of polyhydroxy-acids are formed. Methyl alcohol and formic acid are produced, however, in larger quantities. Dextrose, on treatment with zinc, yields formic acid, diacetyl, and methylglyoxal, also polyhydroxy-acids, but no methyl alcohol. S. B. S.

The Depolymerisation of Sugars. Carl Neuberg (*Biochem. Zeitsch.*, 1908, **12**, 337—341).—Pure crystalline glycerose was prepared by the method of Fenton and Jackson, and polymerised by treating with a colloidal solution of barium carbonate in methyl alcohol. By this means a pentose was obtained, as furfuraldehyde could be obtained by distillation of the condensation product with hydrochloric acid, and was isolated in the form of its condensation product with *p*-nitrophenylhydrazine. As pure glycerose was employed, the formation of a pentose from the triose can only be explained by assuming that the latter depolymerises to formaldehyde, an assumption that is rendered probable by the work of Buchner and other investigators.
S. B. S.

Preparation of an Anhydrous Crystalline Compound of Dextrose and Sodium Iodide. Funia Johann A. Wülfing (D.R.-P. 196605).—The compound $2C_6H_{12}O_6,NaI$, octahedral crystals, m. p. 185—186°, is produced by boiling together anhydrous dextrose and sodium iodide in alcoholic solution; it separates on diluting the solution with about 10% of water and allowing to cool. G. T. M.

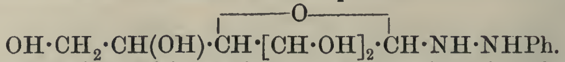
Phenylhydrazones of Dextrose. Robert Behrend and Friedrich Lohr (*Annalen*, 1908, **362**, 78—114).—The compound, m. p. 106—107°, obtained by the action of an alcoholic solution of phenylhydrazine on dextrose, either in the solid state or in strong aqueous solution, and described previously (Abstr., 1907, i, 481) as being identical with Skraup's β-phenylhydrazone, is now shown to be a loose combination of 1 mol. of phenylhydrazine with 2 mols. of a hydrazone, which it is proposed to call dextrose-β-phenylhydrazone. Skraup's β-hydrazone is merely a mixture of this hydrazone with some α-hydrazone. Another compound, containing 1 mol. of phenylhydrazine loosely combined with 1 mol. of the β-hydrazone, has also been isolated. A solution of either of the hydrazones or phenylhydrazine additive compounds in hot pyridine deposits on cooling a pyridine additive compound of the β-hydrazone, from which the pure β-hydrazone is obtained by washing with cold alcohol. It is thus possible to pass from the α- to the β-isomeride.

Solutions of either the α- or β-hydrazone in pyridine, having the approximate initial values $[\alpha]_D$ −87° and −10° respectively, become dextrorotatory when kept for some time. If these solutions are heated at 80—85° for about one and a-half hours and then cooled rapidly, the value observed in each case is roughly $[\alpha]_D$ +18·5°; the rotation gradually decreases at the ordinary temperature, the final value being roughly $[\alpha]_D$ +5°. All attempts to separate the dextrorotatory isomeride present in these solutions were unsuccessful.

The possible structural formulæ of the isomeric phenylhydrazones are discussed. It is considered probable that the *α*- and *β*-hydrazones are the *syn*- and *anti*-forms of the true hydrazone,

$$\mathrm{OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot CH{:}N\cdot NHPh},$$

or that one of them is a true hydrazone, whilst the other is one of the possible stereoisomeric forms of the compound



$$\mathrm{OH\cdot CH_2\cdot CH(OH)\cdot \overbrace{CH\cdot[CH\cdot OH]_2\cdot CH}^{O}\cdot NH\cdot NHPh}.$$

The velocity with which one isomeride passes into the other in solution is increased by traces of acid and diminished by alkalis. The equilibrium mixture of the two hydrazones in aqueous solution has the optical rotatory power $[\alpha]_D^{19}$ −53·74°.

The *substance*, $(C_6H_{12}O_5{:}N\cdot NHPh)_2,NHPh\cdot NH_2$, previously described as dextrose-*β*-phenylhydrazone (*loc. cit.*), is best prepared by the action of phenylhydrazine on dextrose in dilute aqueous alcoholic solution; traces of ammonia retard the formation of this substance to a great extent. The same compound is also formed by the action of an alcoholic solution of phenylhydrazine on either solid *α*- or *β*-dextrose. An aqueous solution (2—4%) ten minutes after dissolving the substance gave $[\alpha]_D$ −4·4°, the final value being $[\alpha]_D$ −48·2°.

The *substance*, $C_6H_{12}O_5{:}N\cdot NHPh,NHPh\cdot NH_2$, prepared by the action of phenylhydrazine (3 parts) on dextrose (1 part), crystallises in concentric groups of large, white prisms, which sinter at about 80°, m. p. 85—87°; a 4% aqueous solution ten minutes after dissolving the substance gave $[\alpha]_D$ −2·82°, the final value being $[\alpha]_D$ −28·45°.

The change in the optical rotatory power of an alcoholic solution with the time is very remarkable; a solution of 0·5017 gram in 25 c.c. gave the following values: $[\alpha]_D$ +3·24°, ±0·00°, −3·49°, −4·99°, ±0·00°, +2·49°, −7·97°, −14·95° at 20, 30, 70, 90 minutes, 4·5, 21·5, 46·5, and 94 hours respectively.

The *pyridine additive compound* of dextrose-*β*-phenylhydrazone, $C_6H_{12}O_5{:}N\cdot NHPh,C_5NH_5$, crystallises in small, colourless, trapezoid plates, m. p. 100—101°. In aqueous solution, the initial value is $[\alpha]_D$ −4·08°, the value after several hours being −38·87°.

Dextrose β-phenylhydrazone, $C_6H_{12}O_5{:}N\cdot NHPh$, is best prepared by treating the pyridine additive compound with small quantities of alcohol. It may also be obtained in the same way from the phenylhydrazine compound, m. p. 107°. It crystallises in small needles, m. p. 140—141°; the optical rotation of an aqueous solution containing a trace of pyridine twenty minutes after dissolution was $[\alpha]_D$ −5·50°, the equilibrium value being $[\alpha]_D$ −53·74°. The *α*-hydrazone crystallises from a solution of the *β*-hydrazone in alcohol containing a small amount of acetic acid at about 20°; the substance, m. p. 106—107°, which separates from the same solution at 0°, and was previously thought to be the *β*-hydrazone, is a mixture of the two isomerides. The *β*-hydrazone may be obtained from the *α*-isomeride by boiling an alcoholic solution of the latter for some time and then rapidly cooling to 0°. W. H. G.

The Precipitation of Sugars by Cupric Hydroxide. S. Yoshimoto (*Zeitsch. physiol. Chem.*, 1908, **56**, 425—445. Compare Salkowski, this Journ., 1872, **25**, 1122; Worm-Müller and Hagen, *Pflüger's Archiv*, 1876, **17**, 568).—Experiments have been made by precipitating cupric hydroxide (from cupric sulphate solution by the addition of sodium hydroxide) in the presence of various sugars. Even when excess of alkali is used, small amounts of sugar are found in the filtrates.

The amount of sugar, however, tends to decrease if the mixture is shaken thoroughly and kept for some little time before filtration.

In the case of all the sugars examined, the amount of sugar left in the filtrate decreases as the amount of alkali is increased, but this value reaches a minimum, and further addition of alkali tends to increase the amount of sugar in the filtrate. With lactose, xylose, and arabinose, the curves are fairly regular, but with dextrose, lævulose, galactose, maltose, sucrose, and raffinose the curves are irregular. In no case is the amount of sugar present in the filtrate directly proportional to the excess of alkali. The minimum has the smallest value in the case of dextrose, namely, 1·66%. J. J. S.

The Molecular Weight of Dextrin from Honey from Coniferous Plants. HERMANN BARSCHALL (*Chem. Zentr.*, 1908, ii, 91; from *Arbb. Kais. Gesundh.-Amt.*, 1908, **28**, 405—419).—The molecular weight of this substance was determined by the cryoscopic method, although it was not found possible to obtain a honey-dextrin free from ash. After the necessary correction for ash has been made, it is found that the value obtained (473) is well above that required for a disaccharide, $(C_5H_{10}O_5)_2 = 324·16$, and falls within the limits of experimental error for a trisaccharide (486·32).

J. V. E.

Action of Nitric Acid on Starch. II. ANTONY G. DOROSCHEWSKY, ADAM W. RAKOWSKY, and A. A. BARDT (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 932—940. Compare Abstr., 1907, i, 678).—In continuation of their previous work, the authors have studied the hydrolysis, by means of 0·4*N* nitric acid, (1) of starch in 8·6% and 14% concentrations, and (2) of starches derived from potatoes, maize, rice, Bermuda arrowroot, and St. Vincent arrowroot.

The results show that in reactions with intermediate stages of the first order, the velocity constant, calculated from the formula for unimolecular reactions, increases slightly as the concentration of the reacting compounds increases. Further, if in these reactions the velocity of the latter stage is much less than that of the first stage, the velocity constant given by the unimolecular formula increases for some time and then remains constant. In particular, a constant velocity-coefficient is obtained when some intermediate stage is taken as the beginning of the reaction.

The velocity constants for the final stage of the hydrolysis of the various starches are: potato, 0·0097; maize, 0·0097; rice, 0·0094; Bermuda arrowroot, 0·0100; St. Vincent arrowroot, 0·0103. The initial stages of the course of hydrolysis vary considerably with the different starches investigated, which may be divided into two groups: (1) rice and maize starches, with which the hydrolysis at first increases, reaching a maximum in about ten minutes; (2) potato and the two arrowroot starches, with which no such increase is observed.

T. H. P.

Action of Nitric Acid on Cellulose. CARL HAEUSSERMANN (*Chem. Zentr.*, 1908, i, 2024; from *Zeitsch. Schiess. Sprengstoffwesen*, 1908, 3, 121—122).—With nitric acid, cellulose yields additive as well as substitution products. Cotton immersed in cold nitric acid, D 1·1—1·45, then pressed, and allowed to dry for three or four days over lime in a vacuum, as described by Knecht (Abstr., 1904, i, 293), gives additive products. This is shown by the fact that cold water removes the acid, and also the bluish-black coloration produced with iodine-potassium iodide solution. When left in the nitric acid, cotton becomes disintegrated, giving soluble substances, amongst which there is scarcely any nitrate. Left in contact with nitric acid of D above 1·45 for a sufficient length of time, cellulose is converted into the nitrate, which is stable towards water, and when free from acid gives no coloration with iodine-potassium iodide solution.

When cellulose fibre is saturated with excess of concentrated acid and the liquid removed before the action is complete, the product gives a blue coloration with iodine-potassium iodide. Cellulose also gives with stronger nitric acid an additive product, which loses water in presence of excess of acid, forming the ester.

J. V. E.

Influence of Sulphuric Acid in Nitration. Especially of Cellulose. CARL KULLGREN (*Chem. Zentr.*, 1908, i, 2024—2025; from *Zeitsch. Schiess. Sprengstoffwesen*, 1908, 3, 146—149. Compare this vol., i, 504).—The author concludes from the results of Schaposhnikoff, Küster and Kremann, Lunge, and others, that the nitric acid is only capable of nitrating when present as the compound HNO_3, and not as hydrate; the part played by the added sulphuric acid being to set free HNO_3 from the hydrate.

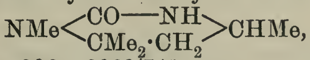
J. V. E.

Two Methods of Preparing Methylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1908, 147, 428—430).—The existing methods of separating ammonia and methylamine are incomplete (compare this vol., i, 505; Bertheaume, this vol., ii, 742). The method of separation by means of yellow mercuric oxide (Abstr., 1907, i, 391) is only applicable to a crude methylamine hydrochloride which contains no other nitrogen base besides ammonia. The crude product obtained in Brochet and Cambier's method (Abstr., 1895, i, 325) of preparing methylamine contains as impurities ammonium chloride, formaldehyde, and trimethyltrimethylenetriamine hydrochloride. The author finds that moderately-concentrated solutions of the latter in hydrochloric acid decolorise a solution of iodine in potassium iodide, afterwards precipitating a brown periodide, and give a pale yellow precipitate with a solution of mercuric iodide in potassium iodide, and that trimethyltrimethylenetriamine hydrochloride is easily soluble in chloroform. By means of these reactions, it is found that Brochet and Cambier's crude hydrochloride, after once recrystallising from alcohol, still contains 3% of the triamine hydrochloride; accordingly, the mercuric oxide separation is inapplicable. On the other hand, the crude hydrochloride resulting from Hofmann's reaction with bromoacetamide contains nothing soluble in chloroform (which dissolves the hydrochlorides of secondary and tertiary bases), and treatment by yellow mercuric oxide gives pure methylamine hydrochloride. The conclusion is drawn that Hofmann's reaction, followed by a separation by mercuric oxide, is the more satisfactory method of preparing pure methylamine. The yield, however, is not good; the author obtained 35% of theory, and probably Hofmann's high apparent yield contained ammonium chloride. E. H.

δ-Amino-β-methylamino-β-methylpentane. MORITZ KOHN and OTTO MORGENSTERN (*Monatsh.*, 1908, **29**, 519—523).—The oxime of methyldiacetonamine, when reduced by sodium and absolute alcohol, yields δ-*amino-β-methylamino-β-methylpentane*,

$$NHMe\cdot CMe_2\cdot CH_2\cdot CHMe\cdot NH_2,$$

b. p. 166—167°, a mobile, fuming liquid with an intense basic odour; the *aurichloride* and *platinichloride* decompose at 215° and 220° respectively, whilst the *picrate* melts in hot water and decomposes at 199—200°. When heated with 1 mol. of ethyl carbonate for thirty hours at 200°, the diamine yields the cyclic *carbamide*,



$$NMe<\begin{matrix}CO\text{---}NH\\CMe_2\cdot CH_2\end{matrix}>CHMe,$$

m. p. 132—133°, b. p. 292—293°/741 mm. C. S.

Preparation of Acylated Aminoalkyl Esters. J. D. RIEDEL (D.R.-P. 194051. Compare Abstr., 1906, i, 631; 1907, i, 897).—*Aminodimethylethylcarbinol*, b. p. 75—80°/30 mm., and the secondary *base*, $NH(CH_2\cdot CMeEt\cdot OH)_2$, b. p. 145°/30 mm., and *hydrochloride*, m. p. 144°, are obtained by heating, at 125°, chlorodimethylethylcarbinol and aqueous ammonia; the former furnishes a *hydrochloride*, leaflets, m. p. 85°, a *di*iso*valeryl* derivative,

$$CMeEt(CH_2\cdot NH\cdot CO\cdot CH_2\cdot CHMe_2)\cdot O\cdot CO\cdot CH_2\cdot CHMe_2,$$

greasy leaflets, m. p. 50°, and a *dibromo*iso*valeryl* derivative,

$$CMeEt(CH_2\cdot NH\cdot CO\cdot CH_2\cdot CMe_2Br)\cdot O\cdot CO\cdot CH_2\cdot CBrMe_2,$$

needles, m. p. 74°.

Phenylaminodimethylcarbinol, $CMePh(CH_2\cdot NH_2)\cdot OH$, b. p. 175°/40 mm., together with the secondary base,

$$NH(CH_2\cdot CMePh\cdot OH)_2,$$

b. p. 258°/40 mm., are obtained by heating, at 125°, phenylchlorodimethylcarbinol and aqueous ammonia; the *dibenzoyl* derivative, prisms, m. p. 110°, is obtained by treating the primary base with benzoyl chloride in pyridine solution. G. T. M.

Preparation of α-Iodo*iso*valerylcarbamide. KNOLL & Co. (D.R.-P. 197648. Compare Abstr., 1907, i, 1017).—*α-Iodo*iso*valerylcarbamide*, leaflets, m. p. 180°, is prepared by heating α-chloro- or α-bromo-*iso*valerylcarbamide with an alkali iodide, or the iodide of an alkaline earth metal, either in alcoholic solution or in the presence of benzene. G. T. M.

Synthesis of α-Aminonitriles. NICOLAI D. ZELINSKY and GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 790—791).—In the formation of the nitriles of α-amino-acids (Abstr., 1906, i, 425) by the action of potassium cyanide (1 mol.) and ammonium chloride (1 mol.) on aldehydes or ketones, the hydrolysis of the potassium cyanide plays an important part, so that the presence of water is necessary in order that the reaction may take place. That this is the case is shown by experiments with benzaldehyde and with *cyclo*hexanone, which yield no nitrile in the absence of water.

T. H. P.

Preparation of Barium Cyanide from Barium Cyanamides. BADISCHE ANILIN & SODA-FABRIK (D.R.-P. 197394).—The reversible reaction $Ba(CN)_2 \rightleftharpoons BaCN_2 + C$ is applied to the production of barium cyanide. The crude product, containing 60% of cyanide and 40% of barium cyanamide, is heated at 600—800° in a stream of acetylene.

A mixture of barium carbonate and wood-charcoal powder is heated in nitrogen at 1500° until no further absorption of gas is observed. The temperature is then lowered to 1100°, and the mixture treated with a current of producer gas previously freed from carbon dioxide until the product is wholly converted into barium cyanide.

G. T. M.

Mercuric Oxycyanide. ERWIN RUPP and S. GOY (*Arch. Pharm.*, 1908, **246**, 367—373. Compare Holdermann, Abstr., 1906, i, 75, 411; Rupp, Abstr., 1906, i, 340).—Mercuric oxide takes part in the formation of the oxycyanide as hydroxide, hence the reaction is accelerated by hydroxyl ions. It is best carried out by mixing 22·2 grams of mercuric oxide in a mortar with 60 c.c. of water and 4 c.c. of 10% sodium hydroxide, adding 27 grams (a slight excess) of mercuric cyanide, and stirring until the mixture is colourless.

Details are also given for the preparation of the oxycyanide from mercuric chloride, mercuric cyanide, and sodium hydroxide, and from alkali cyanide and mercuric chloride. The fact that mercuric salts are not precipitated by sodium hydroxide in the presence of mercuric cyanide depends on the formation of mercuric oxycyanide.

G. B.

Oxidations Effected by Ferric Salts. C. BONGIOVANNI (*Gazzetta*, 1908, **38**, ii, 5—9).—The author produces fresh evidence in support of his view concerning the reaction between ferric chloride and potassium thiocyanate (Abstr., 1907, i, 833). According to Tarugi (Abstr., 1905, i, 176), the red coloration produced in this reaction is due to the formation of the ferrous salt of a peroxythiocyanic acid,

$$FeHC_3O_3N_3S_3,$$

which, like the free acid, is decolorised by dilution or by solutions of oxalates, tartrates, &c., being converted thereby into normal thiocyanic acid or thiocyanate. The author, however, explains the decoloration produced by dilution as due to the hydrolysis of the non-dissociated red, $Fe(CNS)_3$, into yellow, colloidal ferric hydroxide and thiocyanic acid; and the decoloration effected by oxalates, tartrates,

&c., by the formation by these substances of complex ions with the iron of the ferric thiocyanate and consequent displacement of the equilibrium $Fe''' + 3CNS \rightleftarrows Fe(CNS)_3$ in such a manner that the coloured part is diminished in amount. This view is supported by the observation that the substances which decolorise ferric thiocyanate also hinder the displacement of iodine from potassium iodide by ferric salts.

The author also traverses the statement of Tarugi and Revello (*Atti Soc. Chim. Roma*, July, 1907), that ferric chloride exerts an oxidising action on potassium ferrocyanide, so that the interaction of these compounds results in the formation of ferrous oxyferrocyanide and not of ferric ferrocyanide. By means of a special apparatus, the author has carried out this reaction in an atmosphere of nitrogen, thus avoiding, as far as possible, the formation of soluble Prussian blue. By washing the precipitate, precipitating by sodium hydroxide solution, again washing, and dissolving in acid, always in an atmosphere of nitrogen, a solution is obtained which contains only traces of ferrous salt, attributable to secondary reactions. Tarugi and Revello's interpretation of the reaction is hence erroneous. T. H. P.

Ureides and Cyanamides of the Dialkylglycollic Acids. Erik Clemmensen and Arnold H. C. Heitman (*Amer. Chem. J.*, 1908, **40**, 280—302).—The authors have prepared ureides of the dialkylglycollic acid by substituting one or more of the hydrogen atoms in carbamide by the radicle $OH·CR_2·CO$. By the action of carbamide and sodium ethoxide on the esters of the dialkylglycollic acids, ureides of the formula $OH·CR_2·CO·NH·CO·NH·CO·CR_2·OH$ are obtained, but when thiocarbamide or guanidine (as thiocyanate) is substituted for carbamide in this reaction, glycollcyanamides are produced, thus:

$$OH·CR_2·CO_2Et + CS(NH_2)_2 + 2NaOEt = OH·CR_2·CO·NNa·CN + NaSH + 3EtOH,$$

and these cyanamides are converted by boiling with acids or alkalis into the ureides just mentioned. It was found possible, however, to obtain C-*diethylglycollylthiocarbamide*,

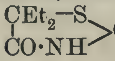
$$OH·CEt_2·CO·NH·CS·NH·CO·CEt_2·OH,$$

by heating a mixture of diethylglycollic acid and thiocarbamide to 180°. At 200°, and with an excess of the latter, *ββ-diethylthiohydantoin* is formed.

C-*Diethylglycollylcarbamide*,

$$OH·CEt_2·CO·NH·CO·NH·CO·CEt_2·OH,$$

forms long, needle-shaped crystals, m. p. 30—31°. In 100 parts of water, 6·5 parts dissolve at 20°, and 14 at 100°. On dry distillation, its salts yield a mixture of diethyl ketone, diethylcarbinol, and probably triethylcarbinol. The *calcium*, *magnesium*, *copper* (normal and acid), *zinc*, *silver*, *mercury*, and double *magnesium-copper* salts are described.

C-*Dipropylglycollylcarbamide* forms a white, crystalline mass, m. p. 39°; the *magnesium* and *mercury* salts are described. C-*Dimethyl glycollylcarbamide* crystallises from light petroleum in white needles, m. p. 74°. It forms double salts of the formula $C_{18}H_{28}O_{10}N_4CuR$ (R = Ca, Ba, Sr, or Mg); the *zinc* and *silver* salts were analysed. C-*Diethyl* *glycollylthiocarbamide* separates from water in long, slender, yellow needles or small, rhombic prisms, m. p. 117—118°. *ββ-Diethylthiohydantoin,*  $\begin{matrix}CEt_2-S \\ | \\ CO\cdot NH\end{matrix}\!\!>C{:}NH$, separates from water in colourless cubes or octahedrons, m. p. 224°. On boiling with barium hydroxide for an hour, it is converted into *diethylthioglycollamide,* $SH\cdot CEt_2\cdot CO\cdot NH_2$, m. p. 147°, and on prolonged boiling it yields *diethylthioglycollic acid,* $SH\cdot CEt_2\cdot CO_2H$, which is being further examined. *Diethylglycollcyanamide,* $OH\cdot CEt_2\cdot CO\cdot NH\cdot CN$, separates from water in shining plates, m. p. 235°. *Dipropylglycollcyanamide* crystallises from water in colourless, monoclinic needles, m. p. 184°. *Dimethylglycollcyanamide* separates from water in tiny, colourless, monoclinic needles, m. p. 248—250°. J. C. C.

Resolution of α-Methyl*iso*serine into its Optically Active Components. FRANCIS W. KAY (*Annalen*, 1908, **362**, 325—332).—α-Methyl*iso*serine is readily resolved in the form of its benzoyl derivative by means of brucine or quinine.

dl-*Benzoyl-α-methyl*iso*serine,* $C_{11}H_{13}O_4N$, prepared by the action of benzoyl chloride and sodium hydroxide on the amino-acid, crystallises in plates, m. p. 153° (corr.). The *brucine* salt of the *d*-compound crystallises from the alcoholic solution of the *dl*-benzoylamino-acid and brucine. d-*Benzoyl-α-methyl*iso*serine,* liberated from its brucine salt by means of sodium hydroxide, crystallises in needles, m. p. 124° (corr.), $[\alpha]_D^{20}$ +9·51°, or, in more dilute solution, $[\alpha]_D^{20}$ +8·40°. l-*Benzoyl-α-methyl*iso*serine,* obtained from the mother liquor of the brucine salts, has $[\alpha]_D^{20}$ −9·23°, or, in more dilute solution, $[\alpha]_D^{20}$ −8·39°, and resembles its optical antipode.

The optically active α-methyl*iso*serines are obtained by hydrolysis of their benzoyl derivatives with boiling hydrobromic acid. The d-*acid,* $C_4H_9O_3N$, when quickly heated, has m. p. about 230° (decomp.), $[\alpha]_D^{20}$ +4·34°. The l-*acid* has $[\alpha]_D^{20}$ −4·15°, and resembles its optical antipode. G. Y.

Resolution of α-Amino-*n*-hexoic Acid into its Optical Components. DEMETRIUS MARKO (*Annalen*, 1908, **362**, 333—337).—α-Amino-*n*-hexoic acid was resolved previously in the form of its benzoyl derivative (Fischer and Hagenbach, Abstr., 1902, i, 85). It is now found better to employ the formyl derivative.

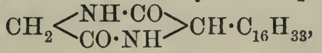
dl-*Formyl-α-amino-*n*-hexoic acid,* $C_7H_{13}O_3N$, prepared by Fischer and Warburg's method (Abstr., 1906, i, 72), crystallises in colourless needles, m. p. 113—115° (corr.). On treatment of the *dl*-compound with brucine in alcoholic solution, the *brucine* salt of the *l*-acid separates, and, on hydrolysis by means of hydrochloric acid, yields l-*formyl-α-amino-*n*-hexoic acid,* which crystallises in silky needles, m. p. 115—118·5° (corr.), $[\alpha]_D^{20}$ −17·56°. The d-*formyl* derivative, obtained from the alcoholic mother liquor, has $[\alpha]_D^{20}$ +17·63°.

The formylamino-acids are hydrolysed by boiling 10% hydrobromic acid. *l*-α-Amino-*n*-hexoic acid, $[\alpha]_D^{20}$ −22·99°; the *d*-acid, $[\alpha]_D^{20}$ +23·14°.

Fischer and Hagenbach (*loc. cit.*) obtained the values $[\alpha]_D^{20}$ $-22{\cdot}4°$ and $+21{\cdot}3°$; by a fermentation process, Schulze and Likiernik obtained an acid having $[\alpha]_D$ $-26{\cdot}5°$. G. Y.

Synthesis of Polypeptides. XXVI. 1. Derivatives of α-Aminostearic Acid. Emil Fischer and Walter Kropp (*Annalen*, 1908, **362**, 338—347).—In comparison with the α-amino-derivatives of the simple fatty acids, the derivatives of the high molecular acids have so far been little studied. As a contribution to the filling of this gap in our knowledge, the authors now describe the combination of glycine with α-aminostearic acid.

Methyl α-aminostearate hydrochloride, $C_{19}H_{40}O_2NCl$, prepared by treating α-aminostearic acid with methyl alcohol and hydrogen chloride, separates from ethyl acetate in needles, m. p. 112° (corr.). The *hydrochloride* of the ethyl ester crystallises in needles, m. p. 89° (corr.).

Methyl chloroacetylaminostearate, $C_{21}H_{40}O_3NCl$, prepared by the successive action of sodium methoxide and chloroacetyl chloride on the hydrochloride of the preceding methyl ester, crystallises from light petroleum in colourless needles, m. p. 78° (corr.). The *ethyl* ester, prepared in the same manner, crystallises in colourless needles, m. p. 68° (corr.). Hydrolysis of the methyl ester with alcoholic sodium hydroxide leads to the formation of *chloroacetylaminostearic acid*, $C_{20}H_{38}O_3NCl$, which crystallises in colourless needles, m. p. 107° (corr.), and, when heated with alcoholic ammonia at 100°, forms *glycyl-α-aminostearic acid*, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(C_{16}H_{33}){\cdot}CO_2H$, crystallising in microscopic prisms, m. p. about 218° (corr.). It dissolves in hot dilute hydrochloric acid or sodium hydroxide, forming frothing solutions; concentrated sodium hydroxide precipitates the *sodium* salt. The *anhydride*,  $CH_2{<}\begin{matrix}NH{\cdot}CO\\CO{\cdot}NH\end{matrix}{>}CH{\cdot}C_{16}H_{33}$, formed by the action of alcoholic ammonia on ethyl chloroacetyl-α-aminostearate at 100°, separates in microscopic crystals, m. p. 219° (corr.), and is insoluble in dilute sodium hydroxide. G. Y.

Synthesis of Polypeptides. XXVI. 2. Derivatives of β-Aminobutyric Acid and of α-Methyl*iso*serine. Francis W. Kay (*Annalen*, 1908, **362**, 348—360).—So far only two polypeptides derived from β-amino-acids, leucyl*iso*serine and *iso*seryl*iso*serine, have been described. As a knowledge of such substances is desirable for the discussion of certain theoretical questions, the author has studied the combinations of *r*-β-aminobutyric acid with *i*-leucine and alanine, and of *r*-α-methyl*iso*serine with *i*-leucine. In the last case both isomeric racemic compounds have been obtained, and are distinguished, as in other similar cases, as the *A* and *B* compounds.

*α-Bromo*iso*hexyl-β-aminobutyric acid*,

$$C_4H_9{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H,$$

prepared by the action of *i*-bromo*iso*hexoyl chloride and sodium hydroxide on β-aminobutyric acid, crystallises in small prisms or needles, m. p. 97—98°; attempts to resolve it into two forms were unsuccessful. The action of 25% aqueous ammonia on the bromo-compound at 25° leads to the formation of *leucyl-β-aminobutyric acid*,

$NH_2 \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CHMe \cdot CH_2 \cdot CO_2H$, which is obtained as a colourless, crystalline powder, m. p. 232° (corr.). The *copper* salt, $(C_{10}H_{19}O_3N_2)_2Cu,CuO$, forms deep blue, six-sided plates. The *anhydride*, $C_{10}H_{18}O_2N_2$, formed by heating the dipeptide at 225°, is obtained as a yellow, sandy powder, m. p. 197—198° (corr.), and is probably quadrimolecular.

Bromopropionyl-β-aminobutyric acid,

$CHMeBr \cdot CO \cdot NH \cdot CHMe \cdot CH_2 \cdot CO_2H$,

prepared from β-aminobutyric acid and bromopropionyl bromide, crystallises from water in colourless needles, m. p. 131° (corr.), and, when treated with aqueous ammonia at 25°, yields *alanyl-β-aminobutyric acid*, $NH_2 \cdot CHMe \cdot CO \cdot NH \cdot CHMe \cdot CH_2 \cdot CO_2H$, which forms an amorphous, slightly grey mass, m. p. about 250° (decomp.), when quickly heated. The *copper* salt, $(C_7H_{13}O_3N_2)_2Cu,CuO,4H_2O$, forms deep blue, six-sided plates.

When coupled with *i*-α-bromo*iso*hexoyl chloride, α-methyl*iso*serine forms two *α-bromo*iso*hexoyl-α-methyl*iso*serines*, $C_{10}H_{18}O_4NBr$. The *A* compound crystallises from the aqueous solution in needles, m. p. 173° (corr.); the *B* compound, obtained from the aqueous mother liquor, crystallises in hexagonal plates, m. p. 125—126° (corr.). *Leucyl-α-methyl*iso*serine A*, $NH_2 \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH_2 \cdot CMe(OH) \cdot CO_2H$, crystallises in microscopic prisms, m. p. about 240° (decomp.); the *phenylcarbimide* derivative, $C_{17}H_{25}O_5N_3$, crystallises in stout prisms, m. p. 180° (corr.). *Leucyl-α-methyl*iso*serine B* crystallises in colourless plates or needles, m. p. 250° (decomp.); the *phenylcarbimide* derivative forms silky needles, m. p. 187° (corr.). G. Y.

Experiments on the Decomposition of Arginine. D. Ackermann (*Zeitsch. physiol. Chem.*, 1908, **56**, 305—315).—The substance described as putridine (*ibid.*, **54**, 24) is now shown to be δ-aminovaleric acid (Salkowski, Abstr., 1898, i, 404). It is thrown down by the reagents usually employed for precipitating alkaloids. When its hydrochloride is heated, it sublimes, and does not yield a ring compound.

Experiments made with the object of proving whether, when arginine undergoes putrefaction, δ-aminovaleric acid is formed, gave negative results. Amongst the products isolated was *r*-ornithine; thus indicating that racemisation had occurred during the reaction. The purification of this base is facilitated by precipitation with mercuric chloride and sodium acetate. Tetramethylenediamine could not be detected.

d-Lysine yields an *aurichloride*, $C_{12}H_{28}O_4N_4,HCl,3HAuCl_4,2H_2O$, which sinters at 120° and melts at 152—155°. The *aurichloride* of the racemic base has the composition $C_{12}H_{28}O_4N_4,4HAuCl_4,H_2O$, and decomposes at 173—176°. The corresponding *platinichloride* crystallises with 1 molecule of alcohol, $C_6H_{14}O_2N_2,H_2PtCl_6,EtOH$, which it loses at 120°. J. J. S.

Derivatives of a Complex Chloride of Gold and Phosphorus. Mario Levi-Malvano (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 847—857).—The author has prepared the following complex compounds of gold and phosphorus:

Aurophosphorous chloride, $(AuPCl_3)Cl$ (compare Lindet, Abstr., 1887, 227). Methyl aurophosphite chloride, $[AuP(OMe)_3]Cl$ (Lindet, *loc. cit.*), which has the molecular weight 384—425 (calc. 356·65) in freezing benzene, and with chloroplatinic acid solutions gives slender, yellow needles of the *platinichloride*, $[AuP(OMe)_3]_2PtCl_6$.

Aurotriethylphosphine chloride, $(AuPEt_3)Cl$, prepared by the action of triethylphosphine on auric chloride dissolved in alcohol, forms colourless needles, m. p. 80°, is stable in the air, and exhibits all the properties of a stable complex salt, since the gold is not precipitated by its ordinary reagents.

Aurotriphenylphosphine chloride, $(AuPPh_3)Cl$, prepared by the interaction of alcoholic solutions of triphenylphosphine and auric chloride, crystallises in colourless, truncated prisms, decomposes at 180—230°, and has the molecular weight 524—532 (calc. 494·6) in freezing benzene. It is stable in the air, and is not dissolved or decomposed by dilute nitric acid, concentrated hydrochloric acid, or potassium hydroxide solution. It forms the *platinichloride*, $(AuPPh_3)_2PtCl_6$, and the *sulphate*, $[AuPPh_3]_2SO_4$.

Methyl auroaminophosphite chloride, $[AuP(OMe)_3(NH_3)_2]Cl$, forms microscopic, prismatic crystals, m. p. 75—76°.

Auroaminotriethylphosphine chloride, $[AuPEt_3(NH_3)_2]Cl$, forms microscopic, colourless prisms, decomposing at 90—150°

Aurotriphenylphosphine chloride is quite insoluble in ammonia.

T. H. P.

Certain Homologues of Naphthalene. GUIDO BARGELLINI and G. MELACINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 26—30).—The two *n*-propylnaphthalenes and the two *n*-butylnaphthalenes are obtained by treating a solution of naphthalene in carbon disulphide with *n*-propionyl chloride or *n*-butyryl chloride in presence of aluminium chloride, separating the isomeric α- and β-ketones thus obtained by means of picric acid, and reducing them with iodide, red phosphorus, and water (compare Claus, Abstr., 1892, 985; 1893, i, 162).

β-Naphthyl propyl ketone crystallises from alcohol in colourless, triclinic plates [A. ROSATI: $a:b:c = 0·6774:1:0·6029$; $\alpha = 94°31'$, $\beta = 140°3·5'$, $\gamma = 90°27'$].

α-n-*Propylnaphthalene*, $C_{10}H_7Pr^a$, prepared by reducing α-naphthyl ethyl ketone, has b. p. 274—275°, and yields a *picrate*, m. p. 141—142°.

β-n-*Propylnaphthalene*, $C_{10}H_7Pr^a$, prepared by the reduction of β-naphthyl ethyl ketone, has b. p. 277—279°, and yields a *picrate*, m. p. 90—92°.

The β-propylnaphthalene prepared by Roux (Abstr., 1888, 1305) by the interaction of *n*-propyl bromide and a carbon disulphide solution of naphthalene in presence of aluminium chloride, is probably β-*iso*-propylnaphthalene, and results in consequence of isomeric change caused by the aluminium chloride.

α-n-Butylnaphthalene, $C_{10}H_7·CH_2Pr^a$, obtained by reducing α-naphthyl propyl ketone, has b. p. 281—283°, and forms a *picrate*, m. p. 104—106°.

β-n-Butylnaphthalene, $C_{10}H_7·CH_2Pr^a$, prepared by the reduction of β-naphthyl propyl ketone, has b. p. 283—285°, and yields a *picrate*, m. p. 71—74°.

The β-butylnaphthalene, b. p. 280°, prepared by Wegscheider (Abstr., 1884, 1185) and by Baur-Thurgau (Abstr., 1894, i, 468) by the action of *iso*butyl chloride or bromide on naphthalene dissolved in carbon disulphide in presence of aluminium chloride, probably contains the tertiary butyl group; its *picrate* has m. p. 96°. T. H. P.

Equilibrium of Hydrogenation. Maurice Padoa and Ugo Fabris (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 125—132. Compare this vol., i, 255).—The authors have made experiments to ascertain whether hydrogenated hydrocarbons, capable of giving up their hydrogen in several stages, can be made to do so by heating in presence of nickel at suitable temperatures.

When phenanthrene is hydrogenated in presence of nickel at 200°, dihydrophenanthrene and tetrahydrophenanthrene are obtained; at 175—200°, α-tetrahydrophenanthrene is formed; at 175°, dodecahydrophenanthrene is given, and at 150° a small quantity of a liquid which does not form a picrate and was not identified (compare Schmidt and Mezger, Abstr., 1907, i, 1022).

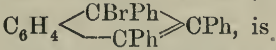
Dodecahydrophenanthrene only loses its hydrogen when heated with nickel at about 220°, at which temperature hexahydrophenanthrene also loses hydrogen, forming gaseous hydrocarbons and β-tetrahydrophenanthrene. At 280°, tetrahydrophenanthrene loses its hydrogen, yielding phenanthrene. In a closed tube at 250°, dodecahydrophenanthrene yields phenanthrene and gaseous hydrocarbons; at 330°, tetrahydrophenanthrene yields dihydrophenanthrene and gaseous hydrocarbons.

When heated in an open tube, decahydronaphthalene begins to lose hydrogen at 250°, naphthalene and gaseous hydrocarbons being formed. In a closed tube at 250°, decahydronaphthalene undergoes little change; at 300°, naphthalene is formed, together with gaseous hydrocarbons. When heated in a closed tube at 250° in presence of nickel, tetrahydronaphthalene is only partially dehydrogenated, gaseous hydrocarbons being formed, and probably also benzene or its homologues.

When decahydrofluorene is heated with nickel in an open tube at 250°, a slow evolution of gas is observed; at 300°, a more copious evolution of gas, mostly hydrogen, occurs. At 300° in a closed tube, hydrogen and gaseous hydrocarbons are evolved.

In an open tube at 250°, *cyclo*hexene gives a large amount of gas, but in a closed tube at the same temperature, very little gas, mainly methane, is formed.

Thus, with hydrocarbons yielding several hydrogenated products, those most readily dehydrogenated by the action of nickel are those containing most hydrogen. Of the hydrocarbons examined, the only ones not attacked in this way are tetrahydronaphthalene at ordinary pressure and tetra- and di-hydrophenanthrene under ordinary or increased pressure. The pressure has a marked influence on the dehydrogenating action of nickel, increased pressure generally causing increased action; with tetrahydronaphthalene, however, hydrogen is eliminated at ordinary pressure, and gaseous hydrocarbons at about three atmospheres pressure. Gradual elimination of the hydrogen of a highly hydrogenated hydrocarbon cannot, as a rule, be effected by gradual rise of temperature; further, the elimination of hydrogen commences only at a temperature considerably higher than that at which the inverse change begins, and is complete, yielding the least highly hydrogenated compound. Hydrogenation and the inverse phenomenon are thus two distinct processes; in some cases, nickel can effect both these changes, but in others, it only acts as a catalyst for the reaction in one direction. With increase of pressure, however, the maximum temperature at which hydrogenation is possible, and the minimum temperature necessary for the inverse change, approach one another, so that hydrogenation becomes possible at temperatures at which it does not take place under ordinary pressure. Under increased pressure, then, the phenomenon becomes one of equilibrium, both hydrogenation and dehydrogenation taking place. Whether the nature of the catalyst influences this equilibrium is unknown. T. H. P.

Triphenylindene and Some of its Derivatives. Elmer P. Kohler (*Amer. Chem. J.*, 1908, 40, 217—233).—In the preparation of diphenylbenzylideneacetophenone by boiling α-bromotriphenylpropiophenone with alcoholic potash (Abstr., 1907, i, 1054), a small amount of 1-*ethoxy*-1 : 2 : 3-*triphenylindene* is produced. This is formed by loss of water from the bromo-ketone and substitution of ethoxyl for bromine in the bromoindene obtained, a process involving the shifting of the bromine atom from the α- to the β-position. 1-*Bromo*-1 : 2 : 3-*triphenylindene*,  $C_6H_4<\begin{matrix}CBrPh\\CPh\end{matrix}>CPh$, is prepared by heating α-bromotriphenylpropiophenone (for which an improved method of preparation is given; compare Abstr., 1906, i, 754) to 150—160°. It separates from ether in large, transparent plates, m. p. 129°, and forms with aluminium bromide a dark red, crystalline *compound*,

$$C_{27}H_{19}Br,AlBr_3.$$

1-*Hydroxy*-1 : 2 : 3-*triphenylindene*, prepared by adding water or sodium acetate to a hot solution of the bromo-derivative in acetic acid, forms lustrous prisms, m. p. 129°; the *methyl* ether crystallises in tablets, m. p. 153°, and the *ethyl* ether separates in large, lustrous prisms, m. p. 172°. On oxidation with a glacial acetic acid solution of chromic acid, the latter furnishes phthalophenone, colourless tablets, m. p. 148° (Zincke, Abstr., 1876, i, 703, gives yellow plates, m. p. 146°). 1 : 2 : 3-*Triphenyl*-1-*ethylindene* is obtained by the action of magnesium ethyl bromide on bromotriphenylindene; it crystallises in plates, m. p. 108°, and, on oxidation with cold chromic and acetic acids, yields *phenyl α-benzoylphenyl-α-phenyl-*n-*propyl ketone*, $C_6H_4Bz\cdot CEtPhBz$, crystallising in large, shining tablets, m. p. 180°, and giving phthalophenone and *o*-benzoylbenzoic acid when boiled with the oxidising agent. When a solution of bromotriphenylindene in benzene is shaken with zinc amalgam and the red solution allowed to evaporate in dry air, *triphenylindenyl peroxide*, $(C_{27}H_{19}O)_2$, is formed. It crystallises in small, shining prisms, decomposing at about 155°. From its sulphuric acid solution, water precipitates some hydroxytriphenylindene and alcohol, ethoxytriphenylindene. 1 : 2 : 3-*Triphenylindene* is prepared by treating an ethereal solution of the bromo-derivative with magnesium and a trace of iodine in an atmosphere of hydrogen and dissolving the excess of magnesium with hydrochloric acid. It crystallises from ether or acetone in large, colourless prisms, m. p. 135°. When treated with bromine vapour at 150—160°, the bromo-derivative is regenerated. On oxidation with chromic and acetic acids, at the ordinary temperature the chief product is the hydroxy-derivative, but when the mixture is boiled, phthalophenone is exclusively formed. 1 : 1 : 3-*Triphenylindene* is the hydrocarbon obtained by Vorländer and Siebert (Abstr., 1906, i, 346) from tetraphenylallene, and the constitution suggested by these authors is now shown to be correct. The oxidation product obtained by them is phthalophenone; when, however, the oxidation with chromic and acetic acids is carried out in the cold, o-*benzoyltriphenylacetic acid*, $C_6H_4Bz\cdot CPh_2\cdot CO_2H$, is formed. This crystallises in small prisms, m. p. 230° (decomp.); the *sodium* salt crystallises in small, colourless prisms, m. p. 130° (decomp.).

J. C. C.

Studies in Nitration. III. Nitration of Aniline and of Certain of its *N*-Alkyl, *N*-Aryl, and *N*-Acyl Derivatives. J. BISHOP TINGLE and F. C. BLANCK (*J. Amer. Chem. Soc.*, 1908, 30, 1395—1412. Compare Abstr., 1907, i, 120; this vol., i, 408).—The authors have extended their work on nitration with 80% nitric acid (D 1·46) in presence of acetic, oxalic, trichloroacetic, or 92% sulphuric acid (D 1·83). Except when sulphuric acid is used, methyl- or ethyl-aniline yields tars, and the formation of tar was the general result of the nitration of dimethyl- or diethyl-aniline under similar conditions. Dimethylaniline, when nitrated in presence of a mixture of oxalic and acetic acid, gives *p*-nitrodimethylaniline. Formanilide yields *p*-nitroformanilide when nitrated in the presence of sulphuric acid, and, under the same conditions, acetanilide gives *m*-nitroacetanilide, but in the presence of oxalic or trichloroacetic acid, *p*-nitroacetanilide is formed. On nitrating benzanilide in the presence of sulphuric acid or a mixture of oxalic and acetic acids, the para-derivative is obtained, but in the presence of acetic acid the meta-derivative results. The products of nitration of a number of other anilides have not yet been identified.

J. C. C.

Iodination of *m*-Nitroaniline by means of Iodine and Potassium Iodate. WILHELM KÖRNER and BELASIO (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 679—690).—*m*-Nitroaniline is readily iodinated by adding iodine dissolved in 25% aqueous potassium hydroxide to a solution of the base in hydrochloric acid containing potassium iodate; using 1 mol. of iodine per mol. of base, a mixed product is obtained containing 8% of 4-*iodo-3-nitroaniline*, 36% 6-*iodo-3-nitroaniline*, 17% 4 : 6-*di-iodo-3-nitroaniline*, and 39% of 2 : 4-di-iodo-3-nitroaniline. The structure of these substances follows from the facts given below.

4-*Iodo-3-nitroaniline* crystallises from alcohol in orange needles, m. p. 142°, and gives an *acetyl* derivative, m. p. 136·5°; the two substances are isomorphous with 4-bromo-3-nitroaniline and its acetyl derivative respectively. On replacing the amino-group by hydrogen, *o*-iodonitrobenzene is obtained; on replacing the same group by iodine, 1:4-di-iodo-2-nitrobenzene (Brenans, Abstr., 1902, i, 673) is formed.

6-*Iodo*-3-*nitroaniline* crystallises from alcohol in orange-yellow needles, m. p. 160·4°, and is convertible into *p*-iodonitroaniline by the diazo reaction. 6-*Iodo*-3-*nitroacetanilide* crystallises from alcohol in slender, white needles, m. p. 199°.

2:4-Di-iodo-3-nitroaniline (Brenans, Abstr., 1904, i, 661), m. p. 125°, gives an *acetyl* derivative crystallising in white, nacreous prisms, m. p. 168°.

4:6-*Di-iodo*-3-*nitroaniline* forms stellate aggregates of slender, pale yellow needles, m. p. 149°, and gives 1:3-di-iodo-4-nitrobenzene on eliminating the amino-group; replacing the same group by iodine, 1:2:4-*tri-iodo*-5-*nitrobenzene*, m. p. 178°, is obtained. This crystallises from carbon disulphide in yellow needles, and, on reduction with ferrous sulphate and ammonia, gives 2:4:5-*tri-iodoaniline*, which crystallises from a mixture of alcohol and ether in long, white, silky needles, m. p. 117·8°, gives an *acetyl* derivative, m. p. 241·5°, and, on eliminating the amino-group, is converted into the 1:2:4-tri-iodobenzene, m. p. 91·4°; the latter substance is also obtained from 1:4-di-iodo-2-nitrobenzene by reduction and the diazo-reaction, thus confirming its structure. The same 1:2:4-tri-iodobenzene can also be obtained from 2:4-di-iodo-3-nitroaniline (supra) by replacing the amino-group by iodine, reducing the nitro-group, and then replacing the amino-radicle by hydrogen.

When 4-iodo-3-nitroaniline is iodinated by means of iodine and potassium iodate, 65% of the product consists of 2:4-di-iodo-3-nitroaniline and 35% of 4:6-di-iodo-3-nitroaniline.

1:2:3-*Tri-iodobenzene* is obtained by converting 2:4-di-iodo-3-nitroaniline into 1:3-di-iodo-2-nitrobenzene (Brenans, *loc. cit.*) by the diazo-reaction, reducing the product to 2:6-*di-iodoaniline*, m. p. 122°, and decomposing the diazo-sulphate derived from the latter by potassium iodide; 1:2:3-*tri-iodobenzene* crystallises in small, white prisms, m. p. 116°.

1:2:4:5-*Tetraiodobenzene*, obtained by replacing the amino-group of 2:4:5-tri-iodoaniline by iodine, crystallises from acetic acid or benzene in white needles, m. p. 254°.

1:3:4-*Tri-iodo*-2-*nitrobenzene*, prepared from 2:4-di-iodo-3-nitroaniline by the diazo-reaction, crystallises from carbon disulphide in long, white prisms, m. p. 137°, and, on reduction with ferrous sulphate and ammonia, gives 2:3:6-*tri-iodoaniline*, crystallising in stellate aggregates of needles and melting at 116·8°. 1:2:3:4-*Tetra-iodobenzene*, obtained from this by the diazo-reaction, crystallises from carbon disulphide and melts at 136°. W. A. D.

[Preparation of 3-Chloro-4-aminodimethylaniline.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197035).—3-*Chloro*-4-*aminodimethylaniline*, white crystals, m. p. 42°, b. p. 158°/15 mm., is prepared by reducing the nitroso-derivative of 3-chlorodimethylaniline; its diazo-salt couples with 1:8-dihydroxynaphthalene-3:6-

disulphonic acid, giving rise to a blue colouring matter. 3-*Chloro-4-aminodimethylaniline*, colourless liquid, b. p. 285°/760 mm., forms a similar blue azo-dye. G. T. M.

Characteristic Colour Reactions Produced by Sodium Hypobromite. William M. Dehn and Silas F. Scott (*J. Amer. Chem. Soc.*, 1908, **30**, 1418—1423. Compare this vol., ii, 907).—Sodium hypobromite solution, either alone or preceded by ammonia, gives characteristic colorations with phenols and aromatic amines. The reactions of a large number of phenols, aromatic amines, and alkaloids are described. Isomeric compounds may readily be distinguished by this means. J. C. C.

Action of Bromine and Chlorine on Phenols. Substitution Products, ψ-Bromides, and ψ-Chlorides. XXIII. Action of Bromine on Di-*p*-hydroxyphenylmethylethylmethane; ψ-Bromides and Quinones of *p-sec.*-Butylphenol. Theodor Zincke and J. Goldemann (*Annalen*, 1908, **362**, 201—220. Compare Zincke and von Hohorst, Abstr., 1907, i, 614).—The interesting results obtained during the investigation on the behaviour of di-*p*-hydroxyphenyldimethylmethane towards bromine (compare Zincke and Grüters, Abstr., 1906, i, 172) have led to a similar investigation on di-*p*-hydroxyphenylmethylethylmethane. The two compounds behave in the same manner; the heptabromide obtained from the higher homologue is, however, far more stable than the corresponding compound derived from the lower homologue.

Di-p-*hydroxyphenylmethylethylmethane*, $CMeEt(C_6H_4{\cdot}OH)_2$, is prepared by the action of hydrogen chloride on a mixture of methyl ethyl ketone (1 part) and phenol (3 parts); it crystallises in colourless needles or prisms, m. p. 124—125°; the *dibenzoate*, $C_{30}H_{26}O_4$, crystallises in white needles, m. p. 140—141°; the *diacetate* could not be obtained in a solid state.

3 : 5 : 3′ : 5′-*Tetrabromo-di*-p-*hydroxyphenylmethylethylmethane*,

$$CMeEt(C_6H_2Br_2{\cdot}OH)_2,$$

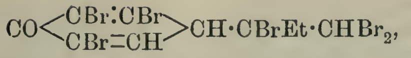
prepared by the action of bromine in glacial acetic acid on the parent phenol, crystallises in thick, white needles, m. p. 155°; the *diacetate*, $C_{20}H_{18}O_4Br_4$, crystallises in white needles, m. p. 174° The tetrabromide is converted by nitric acid (D 1·4—1·5) in acetic acid into 2 : 6-*dibromo*-4-*nitrophenol*, $C_6H_3O_3NBr_2$, m. p. 139—140°, and 2-*bromo*-4 : 6-*dinitrophenol*, pale yellow needles, m. p. 118—119°. Boiling nitric acid converts the tetrabromide into picric acid.

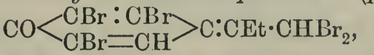
3 : 3′-*Dibromo*-5 : 5′-*dinitro-di*-p-*hydroxyphenylmethylethylmethane*,

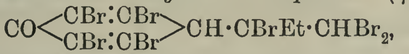
$$C_{16}H_{14}O_6N_2Br_2,$$

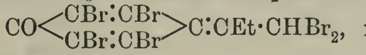
is formed by adding solid sodium nitrite to a solution of the tetrabromide in glacial acetic acid; it forms small, compact, yellow crystals, m. p. 146—147°, and yields soluble, yellowish-red alkali and ammonium salts and insoluble, intensely red barium and calcium salts; the *diacetate*, $C_{20}H_{18}O_8N_2Br_2$, crystallises in yellowish-white needles, m. p. 144—145°.

ψ-p-*Tribromo*-sec.-*butyltribromophenol* (ψ-*hexabromo*-p-sec.-*butyl*-

phenol),  $\mathrm{CO<\substack{CBr:CBr\\ CBr{=}CH}>CH\cdot CBrEt\cdot CHBr_2}$, is formed together with tribromophenol when the tetrabromide described above is treated with bromine at the ordinary temperature; it crystallises in small, colourless, glistening prisms, m. p. 154—155°. *Acetylhexabromo*-p-sec.-*butylphenol*, $C_{12}H_{10}O_2Br_6$, crystallises in colourless prisms, m. p. 142°.

p-*Dibromo*-sec.-*butylidenetribromoquinone* (*pentabromo*-sec.-*butylidenequinone*),  $\mathrm{CO<\substack{CBr:CBr\\ CBr{=}CH}>C:CEt\cdot CHBr_2}$, prepared by shaking an ethereal solution of the hexabromide just described with a 10% aqueous solution of sodium acetate, crystallises in yellow prisms, m. p. 182—183°. It is converted by acetic anhydride and strong sulphuric acid at the ordinary temperature into p-*α-dibromo-β-acetoxy*-sec.-*butyltribromophenyl acetate*, $OAc\cdot C_6HBr_3\cdot CEt(OAc)\cdot CHBr_2$, which crystallises in colourless, glistening prisms or plates, m. p. 164—165°.

ψ-p-*Tribromo*-sec.-*butyltetrabromophenol* (ψ-*heptabromo*-p-sec.-*butylphenol*),  $\mathrm{CO<\substack{CBr:CBr\\ CBr:CBr}>CH\cdot CBrEt\cdot CHBr_2}$, is formed together with tribromophenol by the action of bromine on the tetrabromide described above at 100°; it crystallises in brilliant, colourless needles, m. p. 190—191° (decomp.); the *acetate*, $C_{12}H_9O_2Br_7$, crystallises in colourless, glistening prisms, m. p. 130—131°.

p-*Dibromo*-sec.-*butylidenetetrabromoquinone* (*hexabromo*-sec.-*butylidenequinone*),  $\mathrm{CO<\substack{CBr:CBr\\ CBr:CBr}>C:CEt\cdot CHBr_2}$, may be prepared by shaking an ethereal solution of the heptabromide with an aqueous solution of sodium carbonate, but not sodium acetate; it is obtained in a purer state by boiling a solution of the heptabromide in benzene with anhydrous sodium carbonate; it crystallises in small, yellow prisms, m. p. 174—175°. Acetic anhydride and concentrated sulphuric acid convert it into *α-dibromo-β-acetoxy*-p-sec.-*butyltetrabromophenyl acetate*, $OAc\cdot C_6Br_4\cdot CEt(OAc)\cdot CHBr_2$; it forms small, granular crystals, which soften at 70°, m. p. 90°. W. H. G.

Action of Bromine and Chlorine on Phenols; Substitution Products, ψ-Bromides, and ψ-Chlorides. XXIV. Tetrachloro- and Tetrabromo-dihydroxybenzhydrol and their Transformation Products. THEODOR ZINCKE and E. BIRSCHEL (*Annalen*, 1908, 362, 221—241. Compare preceding abstract).—It has been shown by Zincke and Krügener (Abstr., 1904, i, 401) that a hexabromohydroxybenzylidenequinone can be prepared from 2 : 3 : 5 : 2′: 3′: 5′-hexabromo-4 : 4′-dihydroxybenzhydrol. Attempts were therefore made to prepare, by similar means, a hydroxybenzylidenequinone, but without success, since 4 : 4′-dihydroxybenzhydrol could not be prepared (compare von Baeyer and Burkhardt, Abstr., 1882, 657). 3 : 5 : 3′: 5′-Tetrabromo-4 : 4′-dihydroxybenzhydrol and the corresponding tetrachloro-compound were, however, prepared, and were found to behave like the hexabromo-derivative.

3 : 5 : 3′: 5′-Tetrabromo-4 : 4′-dihydroxybenzophenone has m. p. 225—226°; von Baeyer and Burkhardt give m. p. 213—214° (*loc. cit.*)

It is converted by bromine at 150—160° into pentabromophenol, and by nitric acid in acetic acid into 2-bromo-4 : 6-dinitrophenol. 3 : 3′-*Dibromo*-5 : 5′-*dinitro*-4 : 4′-*dihydroxybenzophenone*, $C_{13}H_6O_7N_2Br_2$, is prepared by adding solid sodium nitrite to a solution of the tetrabromide in glacial acetic acid; it crystallises in yellow needles, m. p. 246°, and forms orange alkali salts; the *diacetate*, $C_{17}H_{10}O_9N_2Br_2$, forms small, compact, pale yellow crystals, m. p. 165°.

3 : 5 : 3′ : 5′-*Tetrachloro*-4 : 4′-*dihydroxybenzophenone*,

$$\mathrm{CO(C_6H_2Cl_2\cdot OH)_2},$$

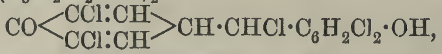
obtained by passing chlorine into a solution of 4 : 4′-dihydroxybenzophenone in acetic acid, crystallises in colourless leaflets or needles, m. p. 231—232°; the *diacetate*, $C_{17}H_{10}O_5Cl_4$, forms slender needles, m. p. 196—197°.

3 : 5 : 3′ : 5′-*Tetrabromo*-4 : 4′-*dihydroxybenzhydrol*,

$$\mathrm{CH(C_6H_2Br_2\cdot OH)_2\cdot OH},$$

is obtained by reducing the tetrabromodihydroxybenzophenone with zinc dust and acetic acid; it crystallises in colourless needles, m. p. 173—174° (decomp.), and is oxidised by bromine or calcium hypobromite to the parent substance.

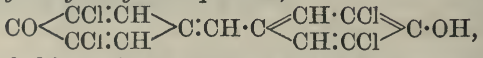
3 : 5 : 3′ : 5′-*Tetrachloro*-4 : 4′-*dihydroxybenzhydrol*, $C_{13}H_8O_3Cl_4$, crystallises in small, compact needles, m. p. 179° (decomp.); the *triacetate*, $C_{19}H_{14}O_6Cl_4$, crystallises in small, glistening plates, m. p. 123—124°. Tetrachlorodihydroxybenzhydrol is converted by a solution of hydrogen chloride in glacial acetic acid into *ψ-pentachloro*-p-*dihydroxydiphenylmethane*, $\mathrm{CHCl(C_6H_2Cl_2\cdot OH)_2}$ or



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CCl{:}CH}\\ \mathrm{CCl{:}CH}\end{matrix}{>}\mathrm{CH\cdot CHCl\cdot C_6H_2Cl_2\cdot OH},$$

crystallising in colourless needles, m. p. 134—135°. It is reduced by zinc and hydrogen chloride in ethereal acetic acid to tetrachloro-*p*-dihydroxydiphenylmethane. The *diacetate*, $\mathrm{CHCl(C_6H_2Cl_2\cdot OAc)_2}$, prepared by the action of acetyl chloride on the ψ-pentachloride, crystallises in small, thick, colourless needles, m. p. 93°.

Tetrachlorohydroxybenzylidenequinone,



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CCl{:}CH}\\ \mathrm{CCl{:}CH}\end{matrix}{>}\mathrm{C{:}CH\cdot C}{<}\begin{matrix}\mathrm{CH\cdot CCl}\\ \mathrm{CH{:}CCl}\end{matrix}{>}\mathrm{C\cdot OH},$$

prepared by shaking with warm water a solution of the ψ-pentachloride in a mixture of benzene and light petroleum, is obtained as a red powder, which sinters at 200°, m. p. about 220°. The product so obtained is not quite pure, and apparently contains $1H_2O$, which is slowly liberated in a vacuum at 80—90°; it quickly becomes yellowish-white under the action of light, due to the absorption of water. The *sodium* salt is deep violet.

Tetrachloro-p-*dihydroxydiphenylmethoxymethane*,

$$\mathrm{CH(C_6H_2Cl_2\cdot OH)_2\cdot OMe},$$

is formed by dissolving the ψ-pentachloride described above in methyl alcohol; it crystallises in thick, colourless needles, m. p. 142°; the *diacetate*, $C_{18}H_{14}O_5Cl_4$, forms small prisms or plates, m. p. 155°. The ψ-pentachloride is converted by boiling acetic acid and sodium acetate into *tetrachloro*-p-*dihydroxydiphenylacetoxymethane*,

$$\mathrm{CH(C_6H_2Cl_2\cdot OH)_2\cdot OAc}\,;$$

it forms compact, colourless crystals, m. p. 171° (decomp.); the *sodium* salt is brownish-red with a green reflex.

ψ-Pentabromo-p-*dihydroxydiphenylmethane*, $CHBr(C_6H_2Br_2\cdot OH)_2$, obtained by the addition of hydrogen bromide to the tetrabromodihydroxybenzhydrol described above, crystallises in small, colourless plates, m. p. 164—165°. It is not converted by acetic anhydride into the normal acetyl derivative, but into *tetrabromo*-p-*dihydroxybenzhydrol triacetate*; this substance could not be obtained pure.

Tetrabromohydroxybenzylidenequinone, $O:C_6H_2Br_2:CH\cdot C_6H_2Br_2\cdot OH$, prepared by adding water to a solution of the ψ-pentabromide in acetone, is a red powder, m. p. 205°; the *sodium* salt is deep violet. The tetrabromoquinone, when warmed with aqueous acetone, readily combines with water, forming the corresponding tetrabromodihydroxybenzhydrol. It is also converted by methyl alcohol into *tetrabromodihydroxydiphenylmethoxymethane*, $CH(C_6H_2Br_2\cdot OH)_2\cdot OMe$, colourless crystals, m. p. 143—144°. W. H. G.

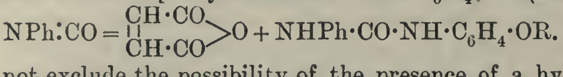
Oxidation of *iso*Eugenol. Dehydrodi*iso*eugenol. HENRI COUSIN and HENRI HÉRISSEY (*Compt. rend.*, 1908, **147**, 247—249; *J. Pharm. Chim.*, 1908, [vi], **28**, 193—199. Compare *ibid.*, **146**, 1413).—When *iso*eugenol (20 c.c.), dissolved in 95% alcohol (180 c.c.), is treated with 40 c.c. ferric chloride solution (D 1·26) and with 120 c.c. of water, the greenish-blue mixture gradually becomes lighter in colour, and deposits light rose-coloured needles, which become colourless when washed with alcohol. The substance crystallises in long, colourless needles or rosettes of flat plates, m. p. 133°, which dissolve in alkali hydroxide solutions. The alcoholic solution gives a greenish-blue coloration with ferric chloride. Results of analysis and a cryoscopic determination of the molecular weight indicate that the substance is *dehydrodi*iso*eugenol*, $C_{20}H_{22}O_4$. The oxidation can be effected with ferric chloride in aqueous solution, but with less satisfactory results, and by the action of a current of air on an aqueous solution of the phenol containing a small proportion of a maceration of *Russula delica* in glycerol.

*Dimethyldehydrodi*iso*eugenol*, obtained by the action of methyl sulphate on the phenol in the presence of potassium hydroxide, crystallises in thin, nacreous, colourless lamellæ, m. p. 126° (corr.).

*Diacetyldehydrodi*iso*eugenol*, prepared by heating dehydrodi*iso*eugenol with acetic anhydride and fused sodium acetate, forms dense, massive, white crystals, m. p. 114° (corr.).

*Dibenzoyldehydrodi*iso*eugenol*, obtained by treating the phenol with benzoyl chloride in the presence of potassium hydroxide, crystallises in spheres of colourless, radiate needles, m. p. 119—120° (corr.).

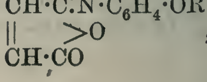
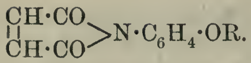
The three ethers are insoluble in water and alkalis, do not give any coloration with ferric chloride, but reduce an aqueous solution of potassium permanganate. E. H.

Maleic and Fumaric Derivatives of *p*-Aminophenols. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 635—641).—In benzene solution, maleic anhydride, like other anhydrides of dibasic acids, reacts with *p*-aminophenols, forming additive compounds, substituted amic acids, which, unlike the corresponding compounds formed with saturated aliphatic and aromatic anhydrides, are yellow and give a violet coloration with ferric chloride in aqueous-alcoholic solution when the hydrogen of the phenolic hydroxyl is replaced by an alkyl radicle. It is hence probable that these amic acids have the enolic constitution $\mathrm{OR\cdot C_6H_4\cdot N{:}C(OH)\cdot CH{:}CH\cdot CO_2H}$. They do not, however, yield substituted carbamates when treated with phenylcarbimide in presence of toluene in the cold, whilst, when heated, decomposition occurs with formation of maleic anhydride and a monosubstituted diphenylcarbamide: $\mathrm{OR\cdot C_6H_4{:}N{:}C(OH)\cdot CH{:}CH\cdot CO_2H} +$  $\mathrm{NPh{:}CO} = \begin{array}{l}\mathrm{CH\cdot CO}\\ \| \qquad\quad >\mathrm{O}\\ \mathrm{CH\cdot CO}\end{array} + \mathrm{NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot OR}$. This reaction does not exclude the possibility of the presence of a hydroxyl group, since hydroxylic compounds are known which do not react with phenylcarbimide, and it is also possible that the above reaction represents the decomposition of the carbamate at the high temperature used.

When maleic anhydride or acid is fused with a *p*-aminophenol at 125—130°, a small quantity of the maleinamate or fumaramate of the aminophenol is formed, together with a large proportion of the corresponding fumaric diamide,

$$\mathrm{OR\cdot C_6H_4\cdot NH\cdot CO\cdot CH{:}CH\cdot CO\cdot NH\cdot C_6H_4\cdot OR}\ (?).$$

These compounds may undergo transformation into the enolic forms, $\mathrm{OR\cdot C_6H_4\cdot N{:}C(OH)\cdot CH{:}CH\cdot C(OH){:}N\cdot C_6H_4\cdot OR}$, and they can, indeed, be obtained in two modifications, one white and the other yellow. But these two forms can be readily converted into one another, the white into the yellow by trituration in a mortar, and the yellow into the white by the addition of water to its sulphuric acid solution, so that they are best regarded as physical or enantiotropic isomerides. That these compounds are fumaric derivatives is shown by the fact that they are also obtained by heating the acid or normal fumarates of the amino-phenols.

When heated, the amic acids obtained from maleic anhydride and *p*-aminophenols yield, not the corresponding imides, but fumaric diamides. The imides of these amic acids, which can be obtained in presence of dehydrating agents, cannot be converted into their enantiotropic forms either mechanically or by crystallisation, and, even at 360°, are not appreciably decomposed or converted into the isomeric compounds. But when the white imides are kept fused at 130—140° in a current of dry carbon dioxide, they are partly transformed into yellow isomeric imides, which have higher melting points than the white modifications, and can be readily obtained by heating the corresponding maleinamino-acids at 170—180° in a stream of dry carbon dioxide. Since mixtures of these imides melt at a lower temperature than either separately, they are not enantiotropic forms, but chemical isomerides. Assuming that the action of acetyl chloride or phosphoryl chloride on amic acids yields asymmetric imides or *iso*-imides (compare Hoogewerff and van Dorp, Abstr., 1893, i, 599; 1894, i, 594), the white imides would have the constitution  $\begin{array}{l}\mathrm{CH\cdot C{:}N\cdot C_6H_4\cdot OR}\\ \| \qquad\quad >\mathrm{O}\\ \mathrm{CH\cdot CO}\end{array}$, and the yellow ones,  $\begin{array}{l}\mathrm{CH\cdot CO}\\ \|\\ \mathrm{CH\cdot CO}\end{array}\!>\mathrm{N\cdot C_6H_4\cdot OR}$. The yellow imides dissolve in alkali alkoxide solutions, giving a faint yellow coloration, whilst the white isomerides yield an intense violet coloration, due to the formation of additive products containing 1 mol. of imide to 1 mol. of alkoxide.

Acetic anhydride decomposes the maleinamic acids into maleic anhydride and acetyl derivatives of the aminophenols. The phenacetin obtained in this way from *p*-ethoxyphenylmaleinamic acid always contains an orange-yellow compound, m. p. 155—157°, with which it forms a solid solution. T. H. P.

Preparation of 2-Aminophenol-5-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 197496).—The sulphonation of *o*-aminophenol with fuming sulphuric acid yields exclusively 2-aminophenol-4-sulphonic acid. An isomeric *2-aminophenol-5-sulphonic acid*, white needles, is obtained by sulphonating carboxy-*o*-aminophenol and hydrolysing the product with aqueous sodium hydroxide. The *diazo*-derivative, yellow needles, is only moderately soluble in water, and. on boiling with alcohol, yields phenol-3-sulphonic acid. G. T. M.

Preparation of Arylsulphonates of 2-Aminophenol-4-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 195226).—*Sodium 4-sulpho-2-nitrophenyl-*p*-toluenesulphonate*,

$$\mathrm{NO_2\cdot C_6H_3(SO_3Na)\cdot O\cdot SO_2\cdot C_7H_7},$$

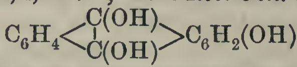
prepared from sodium *o*-nitrophenol-4-sulphonate and *p*-toluenesulphonyl chloride in aqueous sodium hydroxide, crystallises in yellow leaflets. The corresponding *amino*-compound,

$$\mathrm{NH_2\cdot C_6H_3(SO_3Na)\cdot O\cdot SO_2\cdot C_7H_7},$$

leaflets, is obtained by reducing the foregoing compound with iron and dilute acetic acid, and treating the products with sodium carbonate; it forms a very reactive, insoluble diazo-derivative. G. T. M.

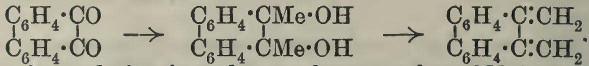
Preparation of 3-Nitro-6-aminophenol-4-sulphonic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 197807).—6-Chloro-2-aminophenol-4-sulphonic, 2-amino-*o*-cresol-4-sulphonic, and 2-amino-*p*-cresol-2-sulphonic acids readily yield carbonyl derivatives on treatment with carbonyl chloride in alkaline solutions. The *sodium* salts of these carbonyl compounds are colourless, soluble, crystalline substances, which, on nitration, furnish nitro-derivatives containing the nitro-group in the para-position to the amino-group. These products, on hydrolysis with aqueous calcium hydroxide, give rise to *2-chloro-3-nitro-6-aminophenol-4-sulphonic*, *6-nitro-3-amino-*o*-cresol-5-sulphonic*, and *2-nitro-5-amino-*p*-cresol-3-sulphonic acids*, which form yellow, soluble alkali salts and diazo-derivatives. G. T. M.

Preparation of the Leuco-derivative of Colouring Matter obtained by Oxidation from 3-Hydroxy-(1)-thionaphthens. KALLE & Co. (D.R.-P. 196501).—When reduced with alkali hyposulphite or dextrin, the colouring matter derived from 3-hydroxy-(1)-thionaphthen furnishes a leuco-derivative, soluble in alkalis, but precipitated by acids. The leuco-compound is sparingly soluble in water, and oxidises only slowly to the colouring matter on exposure to the atmosphere; it forms a soluble sodium salt, crystallising in lustrous, colourless leaflets. G. T. M.

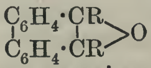
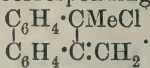
Leucoalizarin (1:2-Dihydroxyanthranol). Eugène Grandmougin (*Chem. Zentr.*, 1908, i, 2179; from *Rev. Gén. Mat. color.*, 1908, 12, 44).—This substance,  $C_6H_4\left\langle\begin{matrix}C(OH)\\|\\C(OH)\end{matrix}\right\rangle C_6H_2(OH)_2$, is prepared by reducing alizarin in very dilute sodium hydroxide solution by means of sodium hydrogen sulphite; it crystallises in small, brown plates, m. p. 150°. J. V. E.

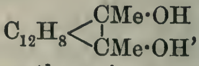
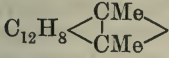
Preparation of *o*-Nitrosobenzyl Alcohol and Anthranil. Kalle & Co. (D.R.-P. 194811).—*o*-Nitrotoluene when heated with aqueous sodium hydroxide at 170°, and subsequently distilled, furnishes an oil which, on treatment with alcoholic mercuric chloride, gives rise to a white, flocculent precipitate, which probably consists of the mercurichloride of o-*nitrosobenzyl alcohol*, from which the latter substance can be liberated by the successive action of concentrated hydrochloric acid and water. The filtrate from the foregoing precipitate contains anthranil, which is set free by strong hydrochloric acid from the concentrated solution. G. T. M.

Ditertiary Alcohols from Phenanthraquinone. Theodor Zincke and W. Tropp (*Annalen*, 1908, 362, 242—259).—From the investigations of Zincke and Buff (Abstr., 1905, i, 880), it seemed probable that quinonoid hydrocarbons might be obtained from the ditertiary alcohols derived from phenanthraquinone (dihydroxydialkyldihydrophenanthrenes; compare Werner and Grob, Abstr., 1904, i, 864) by the elimination of water:



$$\begin{matrix}C_6H_4\cdot CO\\|\qquad\ |\\C_6H_4\cdot CO\end{matrix}\longrightarrow\begin{matrix}C_6H_4\cdot CMe\cdot OH\\|\qquad\ |\\C_6H_4\cdot CMe\cdot OH\end{matrix}\longrightarrow\begin{matrix}C_6H_4\cdot C{:}CH_2\\|\qquad\ |\\C_6H_4\cdot C{:}CH_2\end{matrix}.$$

The hydroxy-derivatives do not, however, lose $2H_2O$, but pass into oxides with the elimination of $1H_2O$. That the compounds so formed have the formula  $\begin{matrix}C_6H_4\cdot CR\\|\qquad |\\C_6H_4\cdot CR\end{matrix}\!\!>O$ is supported by the fact that they do not yield hydrazones or oximes, and are converted on reduction into 9:10-dialkylphenanthrenes. The latter are oxidised by chromic acid to diketones, $R\cdot CO\cdot C_6H_4\cdot C_6H_4\cdot CO\cdot R$; the same diketones are formed by oxidising the parent dihydroxy-compounds. Dihydroxydimethyldihydrophenanthrene is converted by phosphorus pentachloride into the corresponding oxide and a chloride which probably has the formula  $\begin{matrix}C_6H_4\cdot CMeCl\\|\qquad |\\C_6H_4\cdot C{:}CH_2\end{matrix}$. The analogous ethyl, propyl, and benzyl compounds, when similarly treated, yield only oxides.

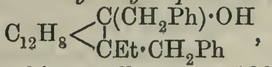
9:10-*Dihydroxydimethyldihydrophenanthrene*,  $C_{12}H_8\left\langle\begin{matrix}CMe\cdot OH\\|\\CMe\cdot OH\end{matrix}\right.$, prepared by adding an ethereal solution of phenanthraquinone to an ethereal solution of magnesium methyl iodide and treating the additive product so formed with dilute sulphuric acid, crystallises in large, colourless, pointed prisms, m. p. 164°; neither an acetyl nor a benzoyl derivative could be prepared. It loses $1H_2O$ when treated with concentrated sulphuric acid in acetic acid, yielding the *oxide*,  $C_{12}H_8<\begin{matrix}CMe\\|\\CMe\end{matrix}>O$, which crystallises in stout, colourless needles or prisms, m. p. 75°. The oxide is reduced by red phosphorus and hydriodic acid to 9 : 10-*dimethylphenanthrene*, $C_{16}H_{14}$, crystallising in colourless, pointed prisms, m. p. 139°. 9 : 10-Dihydroxydimethyldihydrophenanthrene is converted by phosphorus pentachloride into the oxide just described and a *chloride*, $C_{16}H_{13}Cl$, obtained as colourless, spear-shaped crystals, m. p. 155°. It loses hydrogen chloride when heated with an alcoholic solution of potassium hydroxide, yielding a *substance* which crystallises in white needles, m. p. 94—95°.

The following compounds are obtained by the same methods as the corresponding methyl derivatives.

9 : 10-*Dihydroxydiethyldihydrophenanthrene*, $C_{18}H_{20}O_2$, crystallises in microscopic, delicate needles, m. p. 120—122°. The corresponding *oxide*, $C_{18}H_{18}O$, crystallises in large plates or long, thin prisms, m. p. 65°; it yields, on reduction, 9 : 10-*diethylphenanthrene* (?), crystallising in silvery leaflets, m. p. 105—106°.

9 : 10-*Dihydroxydipropyldihydrophenanthrene*, $C_{20}H_{24}O_2$, forms large, hard prisms, m. p. 155—156°. The *oxide*, $C_{20}H_{22}O$, crystallises in prisms, m. p. 83°; it is not reduced by hydriodic acid and red phosphorus.

9 : 10-*Dihydroxydibenzyldihydrophenanthrene*, $C_{28}H_{24}O_2$, crystallises in asymmetric prisms, m. p. 175°. The *oxide*, $C_{28}H_{22}O$, forms compact needles and pointed prisms, m. p. 143°; it is not attacked by phosphorus pentachloride under pressure at 150°, but is reduced by hydriodic acid and red phosphorus at 160° to phenanthrene. The oxide reacts with magnesium ethyl bromide, forming an additive product which, when treated with dilute sulphuric acid, yields 9-*hydroxy*-9 : 10-*dibenzyl*-10-*ethyldihydrophenanthrene*,



$$C_{12}H_8<\begin{matrix}C(CH_2Ph)\cdot OH\\|\\CEt\cdot CH_2Ph\end{matrix},$$

crystallising in slender, white needles, m. p. 186—187°. W. H. G.

Comparative Experiments on the Basicity and Strength of Acids and Phenols. Alfred Thiel and Hermann Römer (*Zeitsch. physikal. Chem.*, 1908, **63**, 711—761. Compare Thiel, Schumacher, and Römer, Abstr., 1906, i, 22).—The method used by the authors consists in studying the changes in conductivity which result from the gradual addition of sodium hydroxide to a standard quantity (generally 1 millimolecule) of an acid in dilute solution (compare Miolati, Abstr., 1900, ii, 214; Küster and Grüters, Abstr., 1903, ii, 611; Küster, Grüters, and Geibel, Abstr., 1905, ii, 55). If the value of the conductivity is plotted against the number of c.c. of sodium hydroxide added, the curve obtained in the case of a strong monobasic acid falls rapidly to a minimum, which coincides with the neutralisation point.

If the monobasic acid is of medium strength, the curve falls a little to a rounded minimum and then rises to the neutralisation point, which is marked by a break in the curve; if the monobasic acid is very weak, no minimum at all is observed, the curve rising from the beginning, and the neutralisation point being marked by a break. It is pointed out that in the case of monobasic acids of medium strength, the weaker the acid the nearer must the minimum lie to the beginning of the curve. Each such acid must at the minimum point be dissociated to the extent of about 15%; the more dilute the solution in which any one such acid is examined the less is the distance between the point of minimum conductivity and the neutralisation point.

The authors discuss also the form of curve which is to be expected when a mixture of two monobasic acids of different strengths or a dibasic acid is gradually neutralised by sodium hydroxide. In the latter case, it is sometimes advantageous to titrate back with a strong acid, as the neutralisation point is then less liable to be obscured by hydrolysis. These more complicated types of curve are illustrated by the authors' experiments with hydrochloric acid + acetic acid, monochloroacetic acid + acetic acid, oxalic, fumaric, maleic, succinic, and phosphoric acids. It is noteworthy that phosphoric acid is found to behave as a dibasic acid (contrast Küster, Grüters, and Geibel, *loc. cit.*).

The authors have made an exhaustive study of the behaviour of aromatic hydroxylic compounds on the lines just indicated, and they draw conclusions as to the way in which the acidic character of the $-OH$ group is modified by the introduction of other substituent groups into the molecule. The following are some of the main conclusions reached.

A compound containing two $-OH$ groups in the *o*-position is monobasic, and the strength is only very slightly greater than that of the corresponding compound with one such group. When the second $-OH$ group is in the meta- or para-position, the substance is dibasic, but the acidic character of the second group is exceedingly feeble. The introduction of nitro-groups markedly increases the acidic power of the $-OH$ group, and the curves obtained by the gradual neutralisation of *o*-nitrophenol, 2:4-dinitrophenol, and picric acid may be taken as examples of the three types mentioned in the beginning of this abstract.

The introduction of a sulphonic group (as in sodium phenolsulphonate) in the ortho- or para-position immensely strengthens the acidic character of the $-OH$ group. In nitro-derivatives of the phenolsulphonic acids, the acidic character of the $-OH$ group is notably greater than in the corresponding nitrophenols. The $-CHO$ group, as shown for example by the behaviour of salicylaldehyde, makes a phenol more distinctly acid. An $-OH$ group in the ortho-position to a carboxyl group is indifferent; in the meta- and para-positions it has an appreciably acid character. For further information as to the influence of these substituents on the acidic character of one or more $-OH$ groups, the original must be consulted.

In one or two favourable cases where the phenolic substance is an acid of medium strength, it is possible to calculate its dissociation constant from the position of the point of minimum conductivity. J. C. P.

Influence of Catalytic Agents in Ester Formation. Hydrogen Bromide and Zinc Bromide in the Formation of Ethyl Benzoate. ISAAC K. PHELPS, M. A. PHELPS, and E. A. EDDY (*Amer. J. Sci.*, 1908, [iv], 26, 281—289).—The rate of esterification of benzoic acid by ethyl alcohol in presence of hydrogen chloride and hydrogen bromide has been studied by Goldschmidt (Abstr., 1896, i, 229) at a temperature of 25°. The results obtained at this temperature were so nearly alike that the conclusion was drawn that hydrogen chloride and hydrogen bromide are of equal efficiency under the conditions of the experiments. Goldschmidt and Sunde (Abstr., 1906, ii, 219) and other authors have recorded physico-chemical measurements which seem to indicate that the efficiency of a catalytic agent depends on its concentration and its degree of dissociation in alcoholic solution.

In an investigation (this vol., i, 166) on the amount of ethyl benzoate formed from benzoic acid in presence of sulphuric acid, hydrogen chloride, or hydrogen chloride and zinc chloride as catalytic agents, with different quantities of alcohol acting for different lengths of time, it was found that the amount of ester produced was increased by increasing the concentration of the catalysts up to a certain limit, but that beyond this point the quantity was decreased. It was also found that the yields of ester did not bear any relation to the degree of ionisation of the catalyst. In the present paper, the catalytic action of hydrogen bromide alone and in presence of zinc bromide at different temperatures on the formation of ethyl benzoate is compared with that of hydrogen chloride and zinc chloride.

The results show that hydrogen bromide varies in its efficiency as a catalytic agent according to its concentration and the temperature at which esterification takes place. The amount of ethyl benzoate formed increases with the time of reaction. Zinc bromide also exerts a catalytic action. The greater the amount of either catalyst present, the greater is the yield of ester. It is found that esterification is retarded by raising the temperature above a certain point, and that a similar effect is produced when hydrogen chloride and zinc chloride are employed, but in this case only at such temperatures as are most unsuitable for esterification. The failure of zinc bromide to act efficiently at the higher temperatures is due to the action of hydrogen bromide on alcohol to form ethyl bromide and water. Hydrogen chloride is therefore more efficient than hydrogen bromide as a catalyst for esterification, although, as Goldschmidt has shown, at as low a temperature as 25°, they are of equal efficiency. The amount of ester produced is not proportional to the concentration of the hydrogen ions. Although, in all cases, the esterification proceeds more completely as the amount of the catalytic agent is increased up to a certain limit, any further increase causes a reduction in the quantity of ester produced. This seems to be due to the fact that all the catalysts employed have a strong affinity for water, and consequently, when they are present in large quantities, absolute alcohol is not able to effect dehydration as thoroughly as is necessary for complete esterification.

E. G.

Influence of Catalytic Agents in Ester Formation. Effect of Certain Sulphates on Benzoic and Succinic Acids. Isaac K. Phelps, H. E. Palmer, and R. Smillie (*Amer. J. Sci.*, 1908, [iv], 26, 290—295).—It has been shown previously (Abstr., 1907, i, 823; this vol., i, 166) that almost theoretical yields of ethyl succinate can be obtained by the action of hydrogen chloride and alcohol on succinic acid, and that quantitative yields of ethyl benzoate can be obtained from benzoic acid when sulphuric acid is used as a catalytic agent. Bogojawlensky and Narbutt (Abstr., 1905, i, 864) have investigated the influence of various inorganic sulphates on the esterification of certain organic acids.

In the present paper, the effect of the hydrogen sulphates of potassium, ammonium, sodium, pyridine, and aniline on the esterification of benzoic and succinic acids is recorded, and the results are compared with those obtained with sulphuric acid. It is found that none of these acid sulphates is so efficient as sulphuric acid. The sodium salt is nearly equal as a catalyst, the ammonium salt is less efficient, the potassium salt considerably less, whilst the pyridine and aniline salts are very poor catalysts. The pyridine salt is more efficient than the aniline salt in the esterification of succinic acid, but in the case of benzoic acid they produce nearly equal effects.

The catalytic action of these sulphates might be due to the dissociation of the sodium and potassium salts into the neutral sulphates and sulphuric acid, and of the pyridine and aniline sulphates into the free base and sulphuric acid, but this explanation fails in the case of the latter salts. Since, in most cases, the salt does not go into solution and an increase in the quantity of salt employed produces a marked effect, it is considered possible that the undissolved salts behave as contact agents. This question is being further investigated.

E. G.

Influence of Catalytic Agents in Ester Formation. Esterification of Benzoic Acid with Certain Chlorides. Isaac K. Phelps, M. A. Phelps, and E. A. Eddy (*Amer. J. Sci.*, 1908, [iv], 26, 296—300).—The catalytic actions at 100—110° of the chlorides of sodium, potassium, lithium, ammonium, copper, calcium, strontium, barium, mercury, aluminium, manganese, tin, lead, antimony and bismuth in presence of small quantities of hydrogen chloride are compared with those of zinc chloride with hydrogen chloride and of hydrogen chloride alone.

The results show that zinc chloride is the most efficient, although copper and tin chlorides are not much less so. The higher chlorides of bismuth, antimony, and mercury are about equally efficient, and nearly as active as zinc, copper, and tin chlorides. Small quantities of calcium chloride are without effect, but large quantities hinder esterification to a marked extent. Strontium chloride retards the action to a smaller degree, and barium chloride hinders esterification but slightly. The chlorides of manganese and potassium, and the lower chlorides of lead and mercury, seem to be without effect. Sodium chloride hinders esterification slightly, lithium chloride more, ammonium chloride still more, and aluminium chloride more than any of the chlorides studied, except calcium chloride when present in large quantities. E. G.

New Method of Preparing Mixed Organic Acid Anhydrides. J. Bougault (*Compt. rend.*, 1908, **147**, 249—251).—It has been shown previously (Abstr., 1905, i, 9; 1906, i, 848; this vol., i, 537) that an aqueous solution of sodium phenyl*iso*crotonate (or generally the salt of any $\beta\gamma$-ethylenic acid) when treated with iodine gives an iodolactone, and that in the presence of a large excess of sodium carbonate the product consists of benzoylacrylic acid (this vol., i, 179, 269). It is now stated that if an aqueous solution of sodium phenyl*iso*crotonate containing excess of sodium carbonate is treated with an equivalent quantity of an aromatic acid and then with iodine, the mixed anhydride of benzoylacrylic acid and the acid added is precipitated. In this manner the following anhydrides have been prepared: *Benzoylacrylic benzoic anhydride*, $COPh\cdot CH{:}CH\cdot CO\cdot O\cdot COPh$, slender colourless needles, m. p. 158°, which are not attacked by cold sodium carbonate solution, but are slowly acted on when heated on a water-bath with the alkali carbonate, acetophenone being evolved. Alkali hydroxide acts more rapidly. Addition of a small quantity of sodium carbonate solution to the boiling alcoholic solution of the anhydride causes the formation of ethyl benzoate. The anhydride is completely hydrolysed by fifteen minutes' boiling with 50% acetic acid. In the presence of zinc, the latter reaction gives benzoic and benzoylpropionic acids. *Benzoylacrylic cinnamic anhydride*, $COPh\cdot CH{:}CH\cdot CO\cdot O\cdot CO\cdot CH{:}CHPh$, has m. p. 154°; *benzoylacrylic phenylacetic anhydride*,

$$COPh\cdot CH{:}CH\cdot CO\cdot O\cdot CO\cdot CH_2Ph,$$

m. p. 118°; and *benzoylacrylic benzoylpropionic anhydride*,

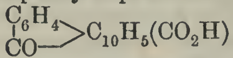
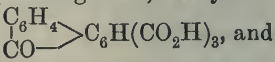
$$COPh\cdot CH{:}CH\cdot CO\cdot O\cdot CO\cdot [CH_2]_2\cdot COPh,$$

m. p. 156°. The essential conditions of the reaction seem to be the insolubility of the anhydride and the nascent state of the benzoylacrylic acid.

The author points out that the exclusion of water and alkali, usually essential to the preparation of anhydrides, is unnecessary in this method. E. H.

Strength of the Second Stage [of the Dissociation] of Phenolcarboxylic and Phenolsulphonic Acids. Alfred Thiel (*Zeitsch. anorg. Chem.*, 1908, 59, 371—372).—In reference to the observations of Ley and Erler (this vol., i, 177) and Obermiller (this vol., i, 634), it is pointed out that, whilst the approximation of the carboxyl group to the phenolic hydroxyl results in a diminution of the acidity of the latter group, the reverse holds good in reference to the influence of the sulphonic group on the acidity of phenolic hydroxyl. As a consequence of this relationship, the strength of the second stage of the hydrogen dissociation of *o*-phenolsulphonic acid is greater than that of *p*-phenolsulphonic acid. H. M. D.

Constitution of 1-Phenylnaphthalene-2:3-dicarboxylic Acid. John E. Bucher (*J. Amer. Chem. Soc.*, 1908, 30, 1244—1264). —Michael and Bucher (Abstr., 1898, i, 256) have shown that by the action of acetic anhydride on phenylpropiolic acid, 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride is produced. This substance has also been studied by Lanser (Abstr., 1899, i, 916), Mauthey (Abstr., 1901, i, 31), and Lanser and Halvorsen (Abstr., 1902, i, 458). Stobbe (Abstr., 1907, i, 769) obtained the anhydride by the action of light on dibenzylidenesuccinic anhydride, and confirmed the constitution assigned to it by Michael and Bucher. In certain points, however, his conclusions differed from those of the latter authors, particularly with reference to the oxidation and reduction of the compound. A brief discussion of Stobbe's results has already been given (Michael and Bucher, this vol., i, 89). The results of a further study are now given in detail and confirm the previous work.

Stobbe (Abstr., 1907, i, 765) has stated that when 1-phenylnaphthalene-2 : 3-dicarboxylic acid is treated with concentrated sulphuric acid, a compound is produced which he termed *allo*chrysoketonecarboxylic acid. It is now shown that this compound is isomeric with 1-phenylnaphthalene-2 : 3-dicarboxylic acid, and has the constitution  $\left.\begin{array}{l}C_6H_4\\ |\\ CO\end{array}\right>C_{10}H_5(CO_2H)$; it melts at 288° without decomposition, and forms potassium and sodium salts containing water of crystallisation. On oxidation with potassium permanganate, it yields a yellow *diphenyleneketonetricarboxylic acid*,  $\left.\begin{array}{l}C_6H_4\\ |\\ CO\end{array}\right>C_6H(CO_2H)_3$, and when fused with potassium hydroxide is converted into a phenylnaphthalenedicarboxylic acid. The diphenyleneketonetricarboxylic acid, on fusion with alkali hydroxide, yields a white *diphenyl*-2 : 3 : 5 : 6′-*tetracarboxylic acid*, $C_6H_2(CO_2H)_3{\cdot}C_6H_4(CO_2H)$, together with a small quantity of diphenyl-2 : 3 : 5 : 6-tetracarboxylic acid.

The action of acetic anhydride on piperonylpropiolic acid, *o*-, *m*-, and *p*-chloro-, *o*- and *p*-bromo-, *m*- and *p*-nitro-, *p*-iodo-, and *p*-methoxyphenylpropiolic acids has been studied. In each case an anhydride is produced which does not reduce alkaline permanganate solution, and is therefore a saturated compound, presumably a derivative of 1-phenylnaphthalene. The constitution of most of these compounds has been proved by transforming them into diphenyltetracarboxylic acid or by oxidising them to benzenepentacarboxylic acid.

*iso*Phthalic and terephthalic acids, when heated with acetic anhydride, are converted quantitatively into the corresponding *anhydrides*, which are almost insoluble in most organic solvents. E. G.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XVIII. Esterification of Dibasic Acids by Diazomethane.

RUDOLF WEGSCHEIDER and HEINRICH GEHRINGER (*Monatsh.*, 1908, 29, 525—530. Compare Abstr., 1907, i, 850).—The acid (2 mols.) and diazomethane (1 mol.) react in ether. The main products are usually the normal ester and unchanged acid; in addition to these, 3-nitrophthalic acid, hemipinic acid, and nitroterephthalic acid yield small quantities of the *a*-methyl ester, whilst 4-hydroxyphthalic acid and camphoric acid give mixtures of the two acid esters. The method is unsuitable for the production of acid esters. C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XIX. Esterification of Phthalonic Acid. Rudolf Wegscheider (*Monatsh.*, 1908, 29, 531—534).—A theoretical discussion of the partial esterification of phthalonic acid, $CO_2H \cdot C_6H_4 \cdot CO \cdot CO_2H$, showing that the aliphatic carboxyl group, being the more strongly acidic, should be first esterified, a result which has been already established by Glogau (Abstr., 1904, i, 673). C. S.

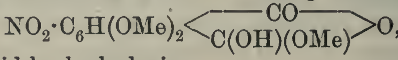
Esterification of Unsymmetrical Di- and Poly-basic Acids. XX. Methyl Esters of 3-Nitrophthalic Acid. Rudolf Wegscheider (*Monatsh.*, 1908, 29, 535—539).—The m. p. of the α-methyl ester of 3-nitrophthalic acid ($CO_2Me:2$), dried at 100°, is given by different investigators as 144—145° or 152—153° (compare McKenzie, Trans., 1901, 79, 1141). The suggestion of decomposition during dehydration is negatived by the fact that, after being maintained at 100° for 363 hours, the ester has practically the same m. p. as after fifteen hours' heating. Rapidity of heating in the m. p. determination or the existence of mixed crystals of the *a* and the *b* methyl esters is not the explanation of the difference. The author suggests the possibility of polymorphism, but satisfactory evidence of it was not obtainable.

The *a* methyl ester, m. p. 149—151°, forms short, monoclinic prisms containing H_2O [$a:b:c=0·5883:1:0·6731$]. The *b* ester ($CO_2Me:1$) forms anhydrous, monoclinic crystals [$a:b:c=0·2678:1:0·2260$]. C. S.

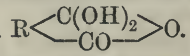
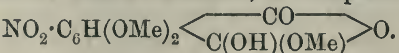
Esterification of Unsymmetrical Di- and Poly-basic Acids. XXI. Nitrohemipinic Acid. Rudolf Wegscheider and Peter von Rušnov (*Monatsh.*, 1908, 29, 541—555).—Of the two carboxyl groups in hemipinic acid (3 : 4-dimethoxybenzene-1 : 2-dicarboxylic acid), that in position 2 is the more strongly acidic and the more subject to steric hindrance. By nitration, a nitro-group enters position 6, and in the resulting nitrohemipinic acid the two preceding characteristics are more pronounced in the carboxyl group in position 1, owing to the influence of the nitro-group. Partial esterification of the two acids by the same method gives, accordingly, acid esters in which different carboxyl groups have been attacked. Both acids yield chiefly the *a* methyl ester by the action of methyl alcohol on the anhydrides or from methyl iodide and the potassium hydrogen salts, whilst the *b* ester is the chief product of esterification by an alcohol and mineral acid. (In accordance with the authors' notation, the more strongly acidic carboxyl group is denoted by *a*; this prefix, therefore, designates different carboxyl groups in the two acids in question.) The neutral esters of the two acids behave differently on partial hydrolysis; whilst dimethyl hemipinate yields entirely the *a* methyl ester, the neutral ester of 6-nitrohemipinic acid, which, contrary to expectation, is obtained without much difficulty by methyl-alcoholic hydrogen chloride, gives about equal quantities of the *a* and the *b* esters. Similarly, hemipinic acid and methyl alcohol at 100° give the *a* ester, whilst nitrohemipinic acid heated with methyl alcohol in an open vessel gives both *a* and *b* esters, the latter in larger amount.

[With Leo Kusy von Dúbrav.]—6-Nitrohemipinic acid, m. p.

155—156° (decomp.), is obtained by oxidising nitro-opianic acid by hot dilute, alkaline potassium permanganate, or, better, by nitrating hemipinic acid in glacial acetic acid at 90—100° by fuming nitric acid. *a-Methyl* 6-*nitrohemipinate* ($CO_2Me:1$) has m. p. 147—149°, and can also be obtained by nitrating *b*-methyl hemipinate. *b-Methyl* 6-*nitrohemipinate* ($CO_2Me:2$) has m. p. 115—117°.

Nitration of *a*-methyl hemipinate gives a *substance*, m. p. 142—144°, not identical with, but of the same composition as, *a*- or *b*-methyl nitrohemipinate. The substance, which is being investigated, is apparently a ψ-ester,  $NO_2{\cdot}C_6H(OMe)_2<\begin{matrix}CO\\C(OH)(OMe)\end{matrix}>O$, since it yields nitrohemipinic acid by hydrolysis. C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXII. Isomerism of Methyl Nitrohemipinates. Rudolf Wegscheider and Hugo Strauch (*Monatsh.*, 1908, 29, 557—572).—ψ-Methyl 6-nitrohemipinate, m. p. 142—144° (preceding abstract), can also be obtained by nitrating either of the polymorphous forms of *a*-methyl hemipinate at 0° without a solvent. A by-product, which becomes the main product when the nitration is performed at 30—50°, is *methyl dinitrodimethoxybenzoate*, m. p. 89—90°, the orientation of which is being investigated.

That the ψ-ester is a derivative of 6-nitrohemipinic acid is proved by hydrolysis, the resulting acid being identical with this acid in all respects. (6-Nitrohemipinic anhydride, obtained by heating the acid at 160—165° in carbon dioxide, has m. p. 155°, not 145° as usually given.) The remarkable fact that 6-nitrohemipinic acid forms three acid methyl esters cannot be explained by polymorphism, since the three esters are precipitated unchanged by acidification of their solutions in alkalis. Experiments for the mutual interconversion of the esters have been unsuccessful. The author revives the old speculation of Roser and Anschütz that dicarboxylic acids may exist in the forms $R(CO_2H)_2$ and  $R<\begin{matrix}C(OH)_2\\CO\end{matrix}>O$. This theory, unnecessary in the case of the great majority of dicarboxylic acids, may serve to account for the occasional abnormally small affinity constants of some dibasic acids and acid esters, and is applicable to opianic and hemipinic acids. The former shows the conductivity of an aldehyde-acid, and yields both normal and ψ-esters. Nitro-opianic acid and its ester exist in the ψ-forms. The nearly related hemipinic acid shows no tendency to exist in the ψ-form. The introduction of the nitro-group, however, increases its tendency to the latter form, so that, whilst nitrohemipinic acid itself has the normal structure, it is capable of yielding a stable ψ-acid ester,  $NO_2{\cdot}C_6H(OMe)_2<\begin{matrix}CO\\C(OH)(OMe)\end{matrix}>O$. C. S.

Synthesis of Some Aromatic Acids. Johan F. Eykman (*Chem. Weekblad*, 1908, 5, 655—666. Compare this vol., i, 22).—A continuation of the author's work on the synthesis of aromatic acids by the action of aromatic hydrocarbons on unsaturated acids in presence of aluminium chloride. Most of the reactions were carried out by maintaining the mixtures at 30° for about four weeks.

β-Phenyl-*n*-butyric acid, $CHPhMe\cdot CH_2\cdot CO_2H$ (Schroeter, Abstr., 1907, i, 531), is obtained from crotonic acid and benzene; it has b. p. 140—145°/3 mm. It crystallises from light petroleum in monoclinic, columnar crystals [$a:b:c=1\cdot22:1:1\cdot08$; $\beta=90\cdot52°$], m. p. 37—38° (Schroeter: 39—40°). The *amide* forms colourless needles, m. p. 106—107°. The *anilide* has m. p. 136—137°. The refractometric constants of the acid are given. Toluene does not yield a similar condensation product with crotonic acid.

α-Phenyl-β-methylbutyric acid, $CHMe_2\cdot CHPh\cdot CO_2H$, is obtained from ββ-dimethylacrylic acid and benzene. It separates from light petroleum in large crystals, m. p. 58—59° (freezing point, 57·4°). The constitution indicated is supported by the fact that the sodium salt has no action on benzaldehyde in presence of either acetic anhydride or the acid chloride, which points to the absence of the group $-CH_2\cdot CO_2H$, and therefore excludes the alternative formula $CPhMe_2\cdot CH_2\cdot CO_2H$. The *amide* has m. p. 68°; the *anilide* 121°. Nitric acid yields a crystalline nitro-acid, m. p. 175° (from alcohol). With toluene, ββ-dimethylacrylic acid yields an *acid*, b. p. 178°/21 mm., which has not been obtained crystalline.

A phenylhydrotiglic acid is formed from tiglic acid and benzene. Crystallised from a mixture of benzene and light petroleum, it has m. p. 132°. Its constitution has not been established, but it may be *α-phenyl-α-methylbutyric acid*, $CPhMeEt\cdot CO_2H$.

αα-Diphenylacetic acid, $CHPh_2\cdot CO_2H$ (compare Symons and Zincke, this Journ., 1874, 162; Friedel and Bahlsohn, Abstr., 1881, 273; Anschütz and Romig, Abstr., 1886, 1033; Zinser, Abstr., 1892, 344; Michael and Jeanprêtre, Abstr., 1892, 1088; Klingemann, Abstr., 1893, i, 590; Fritsch and Feldmann, Abstr., 1899, i, 600), is formed from αα-bromophenylacetic acid and benzene. It separates from a mixture of benzene and light petroleum in crystals, m. p. 148—149°.

Cinnamic acid and benzene yield ββ-diphenylpropionic acid,

$$CHPh_2\cdot CH_2\cdot CO_2H$$

(Henderson, Trans., 1891, 784; Liebermann and Hartmann, Abstr., 1892, 848, 1228), which crystallises from benzene, m. p. 154—155° (corr.). The oxidation of the acid by permanganate to benzophenone, and its formation from ββ-bromophenylpropionic acid, establish its constitution. The *amide* crystallises from benzene in glistening leaflets, m. p. 125—126°; the *anilide* from alcohol, m. p. 177—178°.

αα-Diphenylpropionic acid, $CPh_2Me\cdot CO_2H$ (Thörner and Zincke, Abstr., 1879, 322; Böttinger, Abstr., 1881, 1035), is formed from α-phenylacrylic acid and benzene. It separates from benzene in crystals, m. p. 173—174°. α-Phenylcrotonic acid does not condense with benzene in presence of aluminium chloride.

ββ-Diphenyl-α-methylpropionic acid, $CHPh_2\cdot CHMe\cdot CO_2H$, is prepared from α-methylcinnamic acid and benzene, and separates from benzene in crystals, m. p. 161°. Permanganate oxidises it to benzophenone. The *amide* has m. p. 123°; the anilide 181°. The *methyl* ester is obtained by saturating a solution of the acid in methyl alcohol with hydrogen chloride. After distillation in a vacuum and recrystallisation from light petroleum, it has m. p. 84—85°.

α-Ethylcinnamic acid and benzene yield an acid, which from analogy to that obtained from the corresponding methyl derivative is probably *ββ-diphenyl-α-ethylpropionic acid*, $CHPh_2\cdot CHEt\cdot CO_2H$. Crystallised from benzene, it has m. p. 167—168°. The *amide* has m. p. 150°; the anilide 211°.

αββ-Triphenylpropionic acid, $CHPh_2\cdot CHPh\cdot CO_2H$, is obtained from α-phenylcinnamic acid and benzene. It is freed from a yellow by-product by dissolving in alcohol and saturating with hydrogen chloride. On diluting with water, the bulk of the acid separates unchanged, along with a small proportion of the *ethyl* ester. The mixture is agitated with dilute caustic alkali, the alcoholic solution extracted with ether, and acidified. The pure acid separates in fine, white needles, m. p. 222—223°. After distillation in a vacuum and recrystallisation from alcohol, the ester is obtained in glistening leaflets, m. p. 122—123°. A. J. W.

Oxidation and Reduction of γ-Cyano-βγ-diphenylbutyric Acid. Samuel Avery and Guy R. McDole (*J. Amer. Chem. Soc.*, 1908, **30**, 1423—1425. Compare this vol., i, 343).—Additional evidence of the correctness of the constitution of γ-cyano-βγ-diphenylbutyric acid is afforded by its behaviour on oxidation and reduction. When the acid is oxidised with neutral potassium permanganate, desylacetic acid, $CHPhBz\cdot CH_2\cdot CO_2H$, is obtained, whilst, on reduction with hot sodium ethoxide and subsequent addition of hydrochloric acid, a mixture of βγ-diphenylbutyric acid and the *hydrochloride* of *δ-amino-βγ-diphenylvaleric acid*, white, blunt needles, m. p. 256°, is formed. J. C. C.

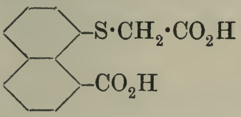
Nitration of β-p-Tolylglutaric Acid. Samuel Avery and Fred W. Upson (*J. Amer. Chem. Soc.*, 1908, **30**, 1425—1429).—When β-*p*-tolylglutaric acid (Avery and Parmelee, Abstr., 1902, i, 679) is added to ten times its weight of fuming nitric acid, 3 : 5-*dinitro-β*-p-*tolylglutaric acid*, pale yellow, microscopic plates, m. p. 182°, is obtained. The *anhydride*, hard, white, glistening plates, has m. p. 230—231°, and gives with aniline the *anilic acid*, white, microscopic needles, m. p. 169—170°. On reduction with ammonium sulphide, the glutaric acid furnishes 3-*nitro*-5-*amino-β*-p-*tolylglutaric acid*, yellowish-brown needles, m. p. 201°, the *silver* salt of which was analysed, and, on oxidation, 3 : 5-dinitroterephthalic acid is formed. The constitution of 3 : 5-dinitro-β-*p*-tolylglutaric acid was proved by the following synthesis: methyl *m*-nitro-*p*-tolylacrylate (Hanzlik and Bianchi, Abstr., 1899, i, 891) is condensed with ethyl malonate, and the product hydrolysed to 3-*nitro-β*-p-*tolylglutaric acid*, m. p. 198·5°. On nitration this yields a dinitro-acid identical with the above. J. C. C

Fixation of Acetophenone by Benzoylacrylic Acid. J. Bougault (*Compt. rend.*, 1908, **147**, 476—478. Compare this vol., i, 179, 269, 422).—When an alkaline solution of benzoylacrylic acid is allowed to remain in the cold for twenty-four hours and then acidified with acetic acid, diphenacylacetic acid is obtained. As von Pechmann found (Abstr., 1882, 1074) that boiling alkalis decompose benzoylacrylic acid with the formation of glyoxylic acid and acetophenone, it is probable that the same reaction proceeds more slowly in the cold, and that the acetophenone formed combines with still undecomposed benzoylacrylic acid in equimolecular proportions. This is proved to be the case by adding acetophenone to an alkaline solution of benzoylacrylic acid, when an increased yield of diphenacylacetic acid, $(CH_2Bz)_2CH\cdot CO_2H$, is invariably obtained. J. C. C.

Preparation of Alkylthiosalicylic [2-Alkylthiolbenzoic] Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 197520).—When *o*-thiocyanobenzoic acid and its derivatives are treated either with alkyl iodides or alkali alkyl sulphates, they yield *o*-alkylthiolbenzoic acids of the general formula $R(S\cdot Alkyl)\cdot CO_2H$.

o-*Methylthiolbenzoic acid*, $C_6H_4(SMe)\cdot CO_2H$, m. p. 168—169°, is obtained by heating together in aqueous sodium hydroxide, *o*-thiocyanobenzoic acid and sodium methylsulphate. o-*Ethylthiolbenzoic acid*, $C_6H_4(SEt)\cdot CO_2H$, m. p. 134—135°, is produced from *o*-thiocyanobenzoic acid, ethyl iodide, and potassium hydroxide in alcoholic solutions; the *ethyl* ester which is first formed is an oil, b. p. 152—153°/10 mm. G. T. M.

[Preparation of 8-Carboxymethylthiolnaphthoic Acid.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 198050).—



8-*Carboxymethylthiolnaphthoic acid*, colourless leaflets, m. p. 175—176°, is prepared by treating the diazo-derivative of 8-aminonaphthoic acid successively with potassium xanthate and sodium chloroacetate. Blue colouring matters are produced by heating this substance with aqueous alkali hydroxides, nitrobenzene, acetic anhydride, acid sulphites, thiosulphates, or sulphur; these dyes are suitable for the hyposulphite vat (compare this vol., i, 451, and preceding abstract). G. T. M.

Preparation of 3-Hydroxy-(1)-thionaphthen-2-carboxylic Acid. KALLE and Co. (D.R.-P. 196016. Compare this vol., i, 451). —A good yield of 3-hydroxy-(1)-thionaphthen-2-carboxylic acid is obtained by heating at 150—200° a mixture of phenylthioglycol-*o*-carboxylic (*o*-carboxymethylthiobenzoic) acid and sodium hydroxide, and acidifying the product at the ordinary temperature. If the mixture becomes heated, carbon dioxide is evolved, and 3-hydroxy-(1)-thionaphthen is produced. G. T. M.

Preparation of Indoxyl and its Derivatives. LEON LILIENFELD (D.R.-P. 195352).—Comparative experiments on Heumann's indigo synthesis have shown that the addition of magnesium powder to the alkali fusion of phenylglycine and its homologues considerably increases the yield of indigotin. Thus a mixture of potassium phenylglycine, sodium and potassium hydroxides, and barium oxide furnished only 27% of indigotin, whereas the addition of magnesium raised the yield to 60%. G. T. M.

Preparation of Tri-, Tetra-, and Hexa-halogenated Derivatives of Indigotin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 195085 and 195291. Compare this vol., i, 695).—*Chlorodibromoindigotin*, $C_{16}H_7O_2N_2ClBr_2$, is obtained by heating chloroindigotin with bromine in nitrobenzene at 226—228°. With a larger proportion of bromine, a chlorotribromoindigotin, $C_{16}H_6O_2N_2ClBr_3$, is produced. These products give leuco-derivatives in the hyposulphite vat, which dye cotton in bright blue shades of extraordinary fastness. *p*-Dichloroindigotin, prepared from 4-chloro-2-aminobenzoic acid, when heated at 225° with bromine in nitrobenzene solution, gives rise to a *dichlorotetrabromoindigotin*, which yields a yellow *leuco*-derivative. When *p*-dibromoindigotin is employed in this reaction, *hexabromoindigotin* is obtained. G. T. M.

Preparation of Succinylsalicylic Acid and its Methyl Homologues. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 196634).—*Succinylsalicylic acid*, $C_2H_4(CO\cdot O\cdot C_6H_4\cdot CO_2H)_2$, white, tasteless, colourless needles, m. p. 176—178°, produced by the interaction of succinyl chloride, salicylic acid, and dimethylaniline in benzene solution, dissolves very sparingly in water, and is only slightly soluble in cold alcohol or glacial acetic acid.

Succinyl-o-*cresotic acid*, $C_2H_4(CO\cdot O\cdot C_6H_3Me\cdot CO_2H)_2$, tasteless, crystalline powder, m. p. 163—164°. *Succinyl*-m-*cresotic acid*, m. p. 195—197°, and *succinyl*-p-*cresotic acid*, colourless crystals, m. p. 193—195°, are prepared by the foregoing reaction, and resemble the preceding compound. G. T. M.

Arylsulphonated Acetonitriles. II. Condensation of the Nitriles with Aromatic Aldehydes and with Amyl Nitrite and Sodium Ethoxide. JULIUS TRÖGER and ADOLF PROCHNOW (*J. pr. Chem.*, 1908, [ii], 78, 123—138).—The similarity between arylsulphonated acetonitriles (Abstr., 1905, i, 336, 870; this vol., i, 633), on the one hand, and ethyl acetoacetate, ethyl cyanoacetate, or benzyl cyanide, on the other, is further illustrated by the readiness with which the nitriles condense with aromatic aldehydes and with amyl nitrite and sodium ethoxide. The RSO_2 group in combination with a nitrile group has much the same effect on the methylene group as carbonyl and carbethoxy radicles. The condensation with aldehydes takes place readily in the presence of a few drops of aqueous sodium hydroxide; the reaction is of the type $R\cdot CH\colon O + R'SO_2\cdot CH_2\cdot CN \rightarrow R\cdot CH\colon C(SO_2R')\cdot CN + H_2O$. The following condensation products (arylsulphonearylideneacetonitriles) have been prepared. The temperatures are melting points:

$R = R' = Ph$, colourless needles, 135°; $R = o\text{-}C_6H_4\cdot OH$, $R' = Ph$, microcrystalline needles, 160°; $R = o\text{-}C_6H_4\cdot OMe$, $R' = Ph$, yellow needles, 113°; $R = p\text{-}C_6H_4\cdot NO_2$, $R' = Ph$, yellow needles, 159°; $R = C_6H_5\cdot CH\colon CH$, $R' = Ph$, yellow needles, 146°; $R = Ph$, $R' = p\text{-}C_6H_4Me$, colourless needles, 114°; $R = o\text{-}C_6H_4\cdot OH$, $R' = p\text{-}C_6H_4Me$, 152°; $R = o\text{-}C_6H_4\cdot OMe$, $R' = p\text{-}C_6H_4Me$, yellow needles, 110°; $R = p\text{-}C_6H_4\cdot NO_2$, $R' = p\text{-}C_6H_4Me$, yellow needles, 198°; R = Ph, R′ = β-$C_{10}H_7$, 122°; R = *o*-C_6H_4·OH, R′ = β-$C_{10}H_7$, microcrystalline needles, 173°; R = *o*-C_6H_4·OMe, R′ = β-$C_{10}H_7$, pale yellow needles, 117°; R = *p*-C_6H_4·NO_2, R′ = β-$C_{10}H_7$, yellow needles, 187°; R = C_6H_5·CH:CH, R′ = β-$C_{10}H_7$, yellow needles, 157°; R = Ph, R′ = *p*-C_6H_4Br, large needles, 119°; R = *o*-C_6H_4·OH, R′ = *p*-C_6H_4Br, needles, 143°; R = *o*-C_6H_4·OMe, R′ = *p*-C_6H_4Br, yellow needles, 146°; R = *p*-C_6H_4·NO_2, R′ = *p*-C_6H_4Br, yellow needles, 210°; R = C_6H_5·CH:CH; R′ = *p*-C_6H_4Br, yellow needles, 176°.

The condensation between the arylsulphonated nitriles, amyl nitrite, and sodium ethoxide may be represented by the equation $C_5H_{11}ONO + RSO_2{\cdot}CH_2{\cdot}CN + NaOEt \longrightarrow C_5H_{11}OH + EtOH + NaO{\cdot}N{:}C(SO_2R)CN$, the methylene hydrogen atoms being replaced by the bivalent oxime group. The free oximes are obtained when the sodium salts are decomposed with hydrochloric acid. The following oximes (*iso*nitroso-compounds) have been prepared: R = Ph, colourless crystals from water, 140°; R = *p*-C_6H_4Me, colourless crystals, 129°; R = β-$C_{10}H_7$, 80°; R = *p*-C_6H_4Br, 163°. J. J. S.

Synthesis and Properties of β-Hydroxy-β-*m*-tolyl-α-ethylpropionic Acid. E. Grishkewitsch-Trochimowsky (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 761—769).—*Ethyl β-hydroxy-β-*m*-tolyl-α-ethylpropionate*, $C_6H_4Me{\cdot}CH(OH){\cdot}CHEt{\cdot}CO_2Et$, prepared by the action of zinc on a mixture of ethyl α-bromobutyrate and *m*-tolualdehyde, is a viscous, colourless liquid, b. p. 187·5—188°/31 mm., and has the normal molecular weight in boiling ether or freezing benzene.

The *acid*, $C_6H_4Me{\cdot}CH(OH){\cdot}CHEt{\cdot}CO_2H$, separates from water in colourless, acicular crystals, m. p. 109·5—110°, and exhibits normal ebullioscopic behaviour in ether. When boiled with 10% sulphuric acid, the acid decomposes in two ways: (1) giving CO_2,H_2O and *α-m-tolyl-Δ^a-butylene*, $C_6H_4Me{\cdot}CH{:}CHEt$, which is a colourless, mobile liquid, b. p. 208°, D^{18} 0·8901, n^{18} 1·5365, and forms the *dibromide*, $C_{11}H_{14}Br_2$; (2) giving *m*-toluic acid, which probably results from *m*-tolualdehyde obtained by decomposition of the acid according to the equation:

$$C_6H_4Me{\cdot}CH(OH){\cdot}CHEt{\cdot}CO_2H = C_3H_7{\cdot}CO_2H + C_6H_4Me{\cdot}CHO.$$

The *potassium*, $C_{12}H_{15}O_3K,H_2O$, *barium*, $(C_{12}H_{15}O_3)_2Ba,8H_2O$, *copper*, *silver*, $C_{12}H_{15}O_3Ag$, *iron*, *lead*, *zinc*, and *platinum* salts of the acid were prepared.

The properties of the acid are compared with those of β-hydroxy-β-*p*-tolyl-α-ethylpropionic acid (compare Mazurewitsch, Abstr., 1907, i, 623). T. H. P.

Action of a Mixture of Ethyl Bromoacetate and *p*-Tolualdehyde on Zinc. Synthesis of β-Hydroxy-β-*p*-tolylpropionic Acid. W. Andriewsky (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 770—782).—*Ethyl β-hydroxy-β-*p*-tolylpropionate*,

$$C_6H_4Me{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2Et,$$

obtained by the action of zinc on a mixture of ethyl bromoacetate and *p*-tolualdehyde, is a yellow, viscous liquid, b. p. 178—180°/19 mm.

The corresponding *acid*, $C_6H_4Me{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$, separates from aqueous alcohol in acicular crystals, m. p. 94—95°, and has the normal molecular weight in boiling ether. The *potassium*, *silver*, and *barium* (+$2H_2O$) salts were analysed, and the ammonium, mercury, zinc, copper, iron, lead, and nickel salts prepared.

When boiled with 10% sulphuric acid solution, the acid is decomposed mainly in accordance with the equation:

$$C_6H_4Me{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H = H_2O + C_6H_4Me{\cdot}CH{:}CH{\cdot}CO_2H,$$

yielding *p*-methylcinnamic acid, a small part of which undergoes further decomposition with formation of *p*-methylstyrene,

$$C_6H_4Me{\cdot}CH{:}CH_2,$$

and carbon dioxide. When subjected to dry distillation at 130°, the acid decomposes into water and *p*-methylcinnamic acid (compare Bronstein, Abstr., 1907, i, 848). T. H. P.

Preparation of Aromatic *o*-Hydroxyaldehydes. HUGO WEIL (D.R.-P. 196239).—A solution of a salicylate when shaken with sodium amalgam shows no apparent change, but when boric acid is first added, the introduction of the amalgam develops immediately an odour of salicylaldehyde.

When *p*-toluidine is also present, *o*-hydroxybenzylidene-*p*-toluidine is produced. The reduction may be carried out electrolytically by using a mercury cathode and a solution containing a sodium salt.

G. T. M.

Derivatives of Phenyl α-Naphthyl Ketone. E. CAILLE (*Bull. Soc. chim.*, 1908, [iv], 3, 916—919).—When an alcoholic solution of phenyl α-naphthyl ketone is treated with sodium amalgam, it yields *phenyl-α-naphthylcarbinol*, which crystallises from alcohol in white, orthorhombic prisms, m. p. 85°, and gives a violet coloration with sulphuric acid; the *benzoyl* derivative, m. p. 106°, crystallises from alcohol in colourless plates, giving a violet coloration with sulphuric acid. The oxime of phenyl α-naphthyl ketone, described by Spiegler (Abstr., 1884, 1182) as a yellow oil, when prepared by the action of hydroxylamine on the ketone, with the addition of zinc chloride, forms white, silky needles, m. p. 73°, and gives an orange coloration with sulphuric acid. The *phenylhydrazone*, m. p. 189°, forms a yellow mass, which reddens on exposure to air and gives a green coloration with sulphuric acid. J. C. C.

Formation of Oximes. UGO GRASSI (*Gazzetta*, 1908, **38**, ii, 32—40).—The formation of *l*-menthoneoxime from *l*-menthone and free hydroxylamine is accelerated by raising the temperature and also by increasing the proportion of alcohol in the solution. In some cases, the optical activity of the solution diminishes considerably instead of increasing, as it should do were the oxime formed. This cannot be due to inversion of the menthone, since the solutions employed were quite neutral to litmus and phenolphthalein, and the proportion of alcohol present was too small to produce rapid inversion. The author therefore assumes the formation of an intermediate compound, which is probably a simple additive compound, $OH{\cdot}CRR'{\cdot}O{\cdot}NH_2$, analogous to those formed by the hydrogen sulphites, or by ammonia with aldehydes, and stable at low temperatures. This compound then passes into the oxime by a process of dehydration, which may well be accelerated by rise of temperature or by alcohol. Some of the solutions of *l*-menthone and hydroxylamine were found to attain a final rotation higher than that calculated for the oxime from the values given by Beckmann (Abstr., 1889, 721).

With regard to the acceleration of the formation of oximes by dehydrating agents, it is found that camphoroxime is formed much more rapidly in absolute alcohol containing anhydrous sodium sulphate than in absolute alcohol alone.

The distribution of hydroxylamine between two ketones has been studied in 94% alcohol at 35°. Under these conditions, hydroxylamine combines with acetone in preference to menthone, but acetone in large excess is unable to remove hydroxylamine from menthoneoxime, at any rate in neutral solutions. Even oximes, such as that of pinacolin, which Stewart's investigations (Trans., 1905, **87**, 185, 410) show to be the weakest, resist energetically the action of other ketones.

T. H. P.

2′ : 4′-Dihydroxyhydrochalkone. GUIDO BARGELLINI and M. MARANTONIO (*Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 119—125).—2′ : 4′-*Dihydroxyhydrochalkone* [o : p-*dihydroxyphenyl phenylethyl ketone*], $CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}C_6H_3(OH)_2$, prepared by the condensation of hydrocinnamic acid and resorcinol in presence of zinc chloride, crystallises from dilute acetic acid in needles, m. p. 88°, dissolves in alkali hydroxide solutions or in concentrated sulphuric acid, giving pale yellow solutions, and in aqueous solution gives a yellow coloration with ferric chloride. The acetyl derivative was obtained as a pale yellow resin which could not be purified. The *monomethyl ether*, $C_{16}H_{16}O_3$, crystallises from water in white needles, m. p. 74—75°, and the *dimethyl ether*, $C_{17}H_{18}O_3$, from dilute acetic acid in long needles, m. p. 103—104°. The *oxime*, $C_{15}H_{15}O_3N$, crystallises from benzene as a white powder, m. p. 171—172°. The ketone is not attacked when heated for several hours with 70% potassium hydroxide solution (compare Weisl, Abstr., 1905, i, 904; Finzi, Abstr., 1905, i, 906).

2′ : 4′-*Dihydroxychalkone* [o : p-*dihydroxyphenyl styryl ketone*],

$$CHPh{:}CH{\cdot}CO{\cdot}C_6H_3(OH)_2,$$

prepared by the condensation of cinnamic acid and resorcinol in presence of zinc chloride, crystallises from water in needles, m. p. 175°.

T. H. P.

Coloured Hydrohalides of Unsaturated Aromatic Ketones. LUIGI FRANCESCONI and G. CUSMANO (*Gazzetta*, 1908, **38**, ii, 70—97).—The authors have prepared a number of aromatic ketones containing various substituent groups and from one to four double linkings in different positions with respect to the carbonyl group. The ketones have been subjected to the action of dry hydrogen chloride, the derivatives obtained being unstable towards water (compare Baeyer and Villiger, Abstr., 1901, i, 659; 1902, i, 355; Vorländer and Mumme, Abstr., 1903, i, 495; Straus and Ecker, Abstr., 1906, i, 859). Certain of the ketones containing three double linkings have been treated with bromine, the addition of which is only partial in some cases and total in others; the behaviour of some of these bromo-derivatives towards hydrogen chloride has been studied.

Methylvanillylideneacetone, $CH_3\cdot CO\cdot CH:CH\cdot C_6H_3(OMe)_2$, prepared by the interaction of methylvanillin and aqueous acetone in presence of sodium hydroxide or by methylating vanillylideneacetone, crystallises from ethyl acetate in yellow needles, m. p. 168°.

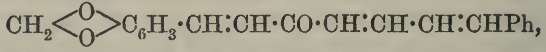
Benzylidenecinnamylideneacetone (compare Scholtz, Abstr., 1896, i, 368) has m. p. 109—110°.

Anisylidenecinnamylideneacetone,

$$OMe\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH:CH\cdot CH:CHPh,$$

separates from a mixture of ether and ethyl acetate in pale yellow crystals, m. p. 138°.

Piperonylidenecinnamylideneacetone,



$$CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH:CH\cdot CO\cdot CH:CH\cdot CH:CHPh,$$

is deposited from ethyl acetate in shining, pale yellow crystals, m. p. 127°.

Methylvanillylidenecinnamylideneacetone,

$$C_6H_3(OMe)_2\cdot CH:CH\cdot CO\cdot CH:CH\cdot CH:CHPh,$$

crystallises from ether in pale yellow leaflets, m. p. 110°.

Salicylidenecinnamylideneacetone,

$$OH\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH:CH\cdot CH:CHPh\ (?),$$

obtained by condensing salicylaldehyde with cinnamylideneacetone in presence of sodium hydroxide, crystallises from chloroform in pale yellow leaflets, m. p. 163°.

Vanillylidenecinnamylideneacetone,

$$OH\cdot C_6H_3(OMe)\cdot CH:CH\cdot CO\cdot CH:CH\cdot CH:CHPh\ (?),$$

obtained only in small quantity, is a pale yellow compound.

It would be expected that ketones of the type

$$CHR:CH\cdot CO\cdot CH:CH\cdot CH:CHR$$

would yield two dibromides, $CHRBr\cdot CHBr\cdot CO\cdot CH:CH\cdot CH:CHR$ and $CHR:CH\cdot CO\cdot CHBr\cdot CH:CH\cdot CHRBr$, and two tetrabromides, $CHRBr\cdot CHBr\cdot CO\cdot CHBr\cdot CH:CH\cdot CHRBr$ and

$$CHR:CH\cdot CO\cdot CHBr\cdot CHBr\cdot CHBr\cdot CHRBr.$$

By the action of two or four atoms of bromine on anisylidenecinnamylideneacetone or piperonylidenecinnamylideneacetone, however, only one di- or tetra-bromide could be isolated. Like the unsaturated aromatic ketones themselves, the dibromides and monohydrobromides of ketones of the type of dibenzylideneacetone give colorations with concentrated sulphuric acid, but no coloration is given by the coloured tetrabromides or dihydrobromides. A coloration is hence only obtained when an ethylene linking is present, and when it is next to the double linking of the carbonyl group. From their ability or inability to give a coloration with sulphuric acid, it is therefore possible to decide the constitution of the tetrahalogenated derivatives, and, since these, with one exception, give no coloration, they must have the structure $CHRBr\cdot CHBr\cdot CO\cdot CHBr\cdot CH:CH\cdot CHRBr$; dibromides of either of the constitutions given above would give a coloration with sulphuric acid, so that in their case the structure cannot be settled.

Anisylidenecinnamylideneacetone dibromide, $C_{20}H_{18}O_2Br_2$, m. p. 135—136° (decomp.), does not increase in weight or become coloured in contact with dry hydrogen chloride, but gives a peacock-blue coloration with concentrated sulphuric acid. The *tetrabromide*, $C_{20}H_{18}O_2Br_4$, m. p. 146—147°, which gradually gives a violet coloration with sulphuric acid, was obtained together with another compound, m. p. 131—133°, the nature of which was not determined. The *hexabromide*, $C_{20}H_{18}O_2Br_6$, separating from ether as a white, microcrystalline powder, m. p. 144°, and gradually giving a violet coloration with sulphuric acid, was obtained together with a whitish-violet, microcrystalline powder, m. p. 172·5°.

Piperonylidenecinnamylideneacetone dibromide, $C_{20}H_{16}O_3Br_2$, separates from chloroform in faintly yellow, microscopic crystals, m. p. 149—150°, and gives an intense coloration with sulphuric acid, but is not affected by hydrogen chloride. The *tetrabromide*, $C_{20}H_{16}O_3Br_4$, m. p. 147—148°, obtained as a white powder becoming faintly rose-red in the light, gives no coloration with either sulphuric acid or hydrogen chloride. The hexabromide could not be prepared, an unsaturated compound derived from the hexabromide by elimination of hydrogen bromide being obtained.

The following hydrochlorides were prepared by the action of dry hydrogen chloride on the various ketones. They are all unstable in presence of water, with which they give the original ketones.

Benzylideneacetone hydrochloride, $C_{10}H_{10}O,HCl$, dense oil; the *dihydrochloride*, $C_{10}H_{10}O,2HCl$, obtained by cooling with ice and salt, forms a dense, reddish-brown oil.

Salicylylideneacetone hydrochloride, $C_{10}H_{10}O_2,HCl$, is a dark reddish-violet oil; the *dihydrochloride*, $C_{10}H_{10}O_2,2HCl$, forms an orange-yellow powder.

Anisylideneacetone hydrochloride, $C_{11}H_{12}O_2,HCl$, is dark green, and the *dihydrochloride*, $C_{11}H_{12}O_2,2HCl$, an orange-yellow powder.

Vanillylideneacetone hydrochloride, $C_{11}H_{12}O_3,HCl$, has a dark peacock-blue colour, and decomposes slowly in the air, giving the ketone.

Methylvanillylideneacetone hydrochloride, $C_{12}H_{14}O_3,HCl$, has a garnet-red colour.

Cinnamylideneacetone hydrochloride, $C_{12}H_{12}O,HCl$, forms a semi-fluid mass with metallic, yellow reflection.

Benzylidenepiperonylideneacetone hydrochloride, $C_{18}H_{14}O_3,2HCl$, resembles colcothar in appearance.

Benzylidenecinnamylideneacetone hydrochloride, $C_{19}H_{16}O,2HCl$, is a peacock-blue compound, and the free ketone dissolves in concentrated sulphuric acid, giving a cochineal-red solution.

Anisylidenecinnamylideneacetone dissolves in concentrated sulphuric acid, giving an intense peacock-blue coloration, and forms two hydrochlorides: the *dihydrochloride*, $C_{20}H_{18}O_2,2HCl$, which is a green powder with metallic lustre, and the *trihydrochloride*, $C_{20}H_{18}O_2,3HCl$, which is dark grey.

Piperonylidenecinnamylideneacetone forms a dark violet solution in sulphuric acid, and yields the *hydrochloride*, $C_{20}H_{16}O_3,2HCl$, m. p. 97° (decomp.), which is a green powder with metallic lustre.

The following general conclusions are drawn from the results obtained by the authors and by Vorländer and Mumme (*loc. cit.*).

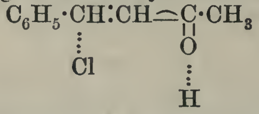
With ketones of the types CHR:CH·CO·R, CHR:CH·CH:CH·CO·R, CHR:CH·CO·CH:CHR, CHR:CH·CH:CH·CO·CH:CHR,

CHR:CH·CH:CH·CO·CH:CH·CH:CHR,

where R represents a substituted aryl or alkyl residue, the number of mols. of hydrogen chloride added at the ordinary temperature is, in general, the same as the number of double linkings in the $\alpha\beta$-position. But the reaction is influenced by the substituent groups of the ketone molecule.

If, in dibenzylideneacetone, which unites readily and in definite molecular proportions with hydrogen chloride, the two hydrogen atoms combined with the carbon atom adjacent to the carbonyl group are replaced by methyl groups, no definite addition of hydrogen chloride occurs either at the ordinary temperature or at 0°. The introduction of methoxyl groups into the ketone molecule also favours the combination with hydrogen chloride. The substituent groups also influence the colour of the hydrochlorides, which, with colourless ketones, are yellow; with yellow ketones containing one double linking and of the type of benzylideneacetone, red, and with ketones containing two or three double linkings, green.

The formation of two series of compounds, one stable and colourless and the other unstable and coloured, by the action of halogen hydracids on unsaturated aromatic ketones cannot be explained either by a difference in the positions assumed by the atoms in the molecule or by a different spacial arrangement of the atoms. The colourless, stable derivatives behave like additive halogen compounds, and are formed according to Thiele's law (Abstr., 1899, i, 554), the application of which to ketones of the types under consideration shows that, if the addition of the hydracid is effected successively, it can only result in the formation of derivatives with one mol. of the acid for ketones with only one double linking and of derivatives with two mols. of acid in the case of ketones with two double linkings. The unstable, coloured additive derivatives are formed by the engaging of the partial valencies due to the double linking, without any movement of the latter, thus:



$$\mathrm{C_6H_5\cdot}\underset{\substack{\vdots\\ \mathrm{Cl}}}{\mathrm{CH}}\mathrm{{:}CH}\simeq\underset{\substack{\| \\ \mathrm{O}\\ \vdots\\ \mathrm{H}}}{\mathrm{C}}\mathrm{\cdot CH_3}$$

These compounds hence represent the first phase of the reaction of addition of the halogen hydracids. T. H. P.

Kawa Root [of Piper methysticum]. E. Winzheimer (*Arch. Pharm.*, 1908, **246**, 338—365).—Besides confirming and extending the results of Pomeranz, the author has mainly investigated the constitution of yangonin. The root contains: resins, 5·3% (of which 23% acids, 77% esters); methysticin, 0·30%; ψ-methysticin, 0·268%; yangonin, 0·184%; an alkaloid, 0·022%; two glucosides, 0·69%; an amorphous acid, insoluble in water, 0·7—0·8%, and sugar. Methysticin has the constitution assigned to it by Pomeranz:

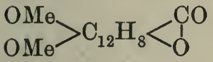
$$CH_2{:}O_2{:}C_6H_3\cdot CH{:}CH\cdot CH{:}CH\cdot CO\cdot CH_2\cdot CO_2Me,$$

or a very similar one, since methysticol, obtained from it, is now proved to be identical with piperonyleneacetone,

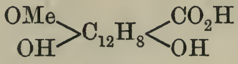
$$CH_2{:}O_2{:}C_6H_3\cdot CH{:}CH\cdot CH{:}CH\cdot CO\cdot CH_3,$$

previously synthesised by Scholtz. The *phenylhydrazone* of methysticol melts at 152—152·5°; the p-*bromophenylhydrazone* at 162—163°; the *semicarbazone* at 199—199·5°; *benzylidenemethysticol*, $C_{20}H_{16}O_3$, at 110—111°; its *phenylhydrazone* at 187·5—188°, and *piperonylidenemethysticol* at 195—195·5°. *ψ-Methysticin* is, like methysticin, an ester of methystic acid; pale yellow leaflets, m. p. 113—114°; the analytical results are doubtful.

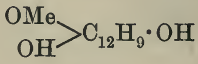
Yangonin (I) has the composition $C_{15}H_{14}O_4$ (and not $C_{17}H_{12}O_5$, or $C_{10}H_8O_3$, as previously supposed). It contains two methoxyl groups, and appears to be a lactone; potassium hydroxide transforms it into *yangonic acid* (II), needles, m. p. 126—126·5°. At its melting point, or in boiling alcohol, this acid loses carbon dioxide, being converted into *yangonol* (III), yellow leaflets, m. p. 92—92·5°. When yangonic acid is heated with acetic anhydride, *acetylyangonic* acid (IV), m. p. 230°, and *acetylyangonic lactone* (V), m. p. 131—132°, are formed.


$\begin{matrix}OMe\\OMe\end{matrix}\!>\!C_{12}H_8\!<\!\begin{matrix}CO\\|\\O\end{matrix}$

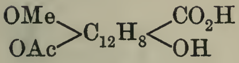
(I.)


$\begin{matrix}OMe\\OH\end{matrix}\!>\!C_{12}H_8\!<\!\begin{matrix}CO_2H\\OH\end{matrix}$

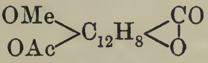
(II.)


$\begin{matrix}OMe\\OH\end{matrix}\!>\!C_{12}H_9\cdot OH$

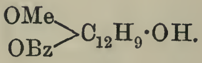
(III.)


$\begin{matrix}OMe\\OAc\end{matrix}\!>\!C_{12}H_8\!<\!\begin{matrix}CO_2H\\OH\end{matrix}$

(IV.)

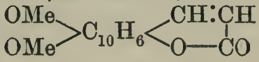

$\begin{matrix}OMe\\OAc\end{matrix}\!>\!C_{12}H_8\!<\!\begin{matrix}CO\\|\\O\end{matrix}$

(V.)


$\begin{matrix}OMe\\OBz\end{matrix}\!>\!C_{12}H_9\cdot OH.$

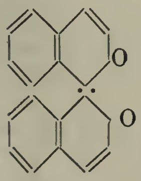
(VI.)

Yangonol forms a *monobenzoyl* derivative (VI), yellow plates, m. p. 103°. On fusion with potassium hydroxide, yangonin yields a small quantity of a crystalline *acid*, m. p. 210—211°, free from methoxyl and probably having the composition $C_{11}H_{10}O_5$. It is regarded as being derived from yangonic acid (like benzoic from cinnamic acid) by the elimination of $-CH\!:\!CH-$; if this is so, the formula for yangonin may be further resolved into

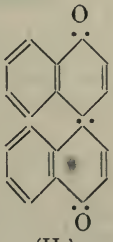

$\begin{matrix}OMe\\OMe\end{matrix}\!>\!C_{10}H_6\!<\!\begin{matrix}CH\!:\!CH\\|\\O\text{—}CO\end{matrix}$

G. B.

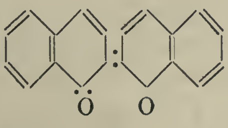
Binuclear Quinones as Chromogens. Herman Decker (*Annalen*, 1908, **362**, 320—324).—Of the six formulæ below, only I, III, and VI can form indigoid dyes according to Friedländer's view of these substances.



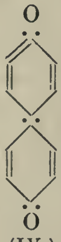
(I.)



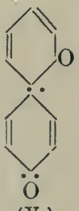
(II.)



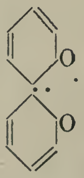
(III.)



(IV.)



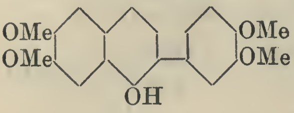
(V.)



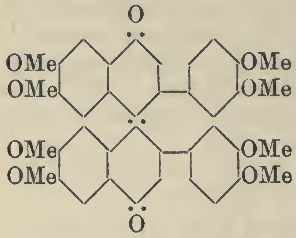
(VI.)

Nevertheless, two strongly coloured derivatives of (II) have now been obtained (see following abstract), and the strong dye, cedriret, is a derivative of (IV). The author proposes therefore to group all such substances under the name of "binuclear quinonoid dyes." The meaning of the term quinonoid must be widened to include substances in which a group, −S−, −O−, −NH−, or −CH_2−, is substituted for −C⁚C−, as also those in which the quinonoid oxygen atom is displaced by a bivalent imine or hydrocarbon group. The binuclear quinonoid dyes fall then into place between the quinonoid and the triphenylmethane dyes. In this new group, the dye and leuco-compounds form two reciprocal systems of conjugated double linkings. G. Y.

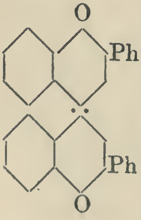
Formation of Naphthol Derivatives from Papaverine and the Binuclear Quinones of the Naphthalene Series. HERMAN DECKER (*Annalen*, 1908, **362**, 305—319).—Decker and Dunant's suggestion that the phenolic compound, m. p. 180°, formed by the action of alkalis on papaverinium methyl haloids, has the annexed constitution (this vol., i, 204) is now confirmed, and the mechanism of the reaction by which it is formed is discussed.



6 : 7-Dimethoxy-2-*mp*-dimethoxyphenyl-α-naphthol gives a light green coloration with sulphuric acid, becoming violet when heated, forms crystalline *alkali* salts, and couples with α-diazonaphthalenes, forming insoluble, brownish-red *azo*-dyes. The *pentamethoxy*-compound, $C_{10}H_4(OMe)_3 \cdot C_6H_3(OMe)_2$, formed by the action of methyl sulphate and alkali on the naphthol, crystallises in white leaflets, m. p. 162—163°, and sublimes unchanged. The blue dye, formed together with tetramethoxyphenylnaphthol by the action of alkalis on papaverinium methyl haloids in presence of air, or by the action of air on the impure naphthol containing veratraldehyde, but not on the pure naphthol or by the action of oxidising agents on the naphthol in alkaline or acid solution, is considered to have the annexed constitution. It is obtained as a dark blue, glistening mass resembling indigotin, m. p. 225—235°, gives a green coloration with concentrated sulphuric acid, is decolorised by hot concentrated or alcoholic potassium hydroxide, and again forms the naphthol when treated with reducing agents.



When boiled with alcoholic potassium hydroxide in an atmosphere of hydrogen in a reflux apparatus, 1-phenyl*iso*quinolinium methiodide evolves methylamine and yields 2-*phenyl-α-naphthol*, which is obtained as a resinous mass, gives the phenol reaction with diazo-solutions, forms a *methyl* and a crystalline *acetyl* derivative, and on oxidation yields a violet *dye*, m. p. about 220°, annexed constitution. This forms a bluish-red solution in alcohol, or a violet-red in benzene or chloroform. G. Y.



The Replacement of a Sulphonic Group by Hydroxyl in Anthraquinone-α-sulphonic Acid and its Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197649).—It has been found that by heating anthraquinone-α-sulphonic acid and its more highly sulphonated derivatives with aqueous sodium carbonate at 190—200°, the sulphonyl groups in α-positions are replaced by hydroxyl. Anthraquinone-1 : 5- and -1 : 8-disulphonic acids yield respectively anthrarufin and chrysazin, with small quantities of 1-hydroxyanthraquinone-5- and -8-sulphonic acids as intermediate products. Anthraquinone-α-sulphonic acid itself furnishes erythrohydroxyanthraquinone. G. T. M.

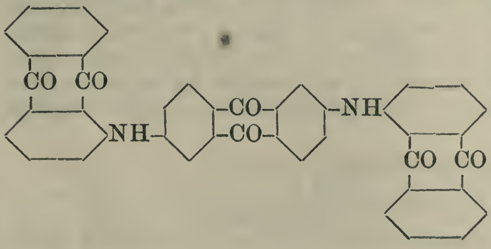
Preparation of Hydroxyanthrarufin and Hydroxychrysazin. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 196980).—1 : 2 : 5-Trihydroxyanthraquinone is readily obtained by heating anthrarufin with a mixture of sodium and potassium hydroxides in the presence of water and sodium nitrate. The employment of the mixture of alkali hydroxides gives a much better result, the oxidation to the trihydroxy-derivative being complete and without production of 1 : 2 : 5 : 6-tetrahydroxyanthraquinone. G. T. M.

Preparation of 1 : 5- and 1 : 8-Hydroxyanthraquinonesulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 197607).—When heated with a mixture of calcium hydroxide and water at 140—150°, 1 : 5- and -1 : 8-anthraquinonedisulphonic acids are readily converted into 1-*hydroxyanthraquinone*-5- and -8-*sulphonic acids*, which are obtained in the form of their sodium salts. G. T. M.

Preparation of Hydroxyanthrarufin and Hydroxychrysazin. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 195028).—1 : 2 : 5-*Trihydroxyanthraquinone* (*hydroxyanthrarufin*), m. p. 273—274°, *triacetyl* derivative, m. p. 228°, was obtained by fusing anthrarufin with sodium nitrate and aqueous sodium hydroxide at 180—185°. 1 : 2 : 8-*Trihydroxyanthraquinone* (*hydroxychrysazin*), orange needles, m. p. 230°, *triacetyl* derivative, m. p. 219°, was obtained under similar conditions from chrysazin. G. T. M.

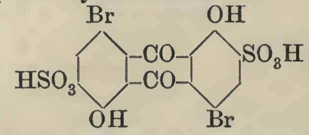
Preparation of Complex Dianthraquinonyldiaminoanthraquinones. BADISCHE ANILIN UND SODA-FABRIK (D.R.-P. 197554. Compare this vol., i, 456).—Complex anthracene colouring matters suitable for vat-dyeing are produced by condensing the amino- and diamino-anthraquinones with *ββ*-dihalogenated anthraquinones containing the two halogen atoms in different rings.

Di-1′-*anthraquinonyl*-2 : 6-*diaminoanthraquinone* is obtained by condensing 2 : 6-dichloroanthraquinone and 1-aminoanthraquinone with anhydrous sodium acetate and cuprous chloride in boiling nitrobenzene. Similar compounds are produced from 2 : 7-dibromoanthraquinone and 1 - aminoanthraquinone,

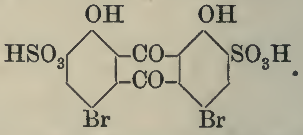


and 2 : 6-dichloroanthraquinone and 1 : 5-diaminoanthraquinone ; they dissolve in concentrated sulphuric acid to green solutions, and furnish yellow or brownish-red leuco-derivatives in the hyposulphite vat. G. T. M.

Preparation of *p*-Dibromoanthrarufin- and Dibromochrysazindisulphonic Acids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 197082).—The sodium hydrogen salts of anthrarufindisulphonic and chrysazindisulphonic acids when treated with bromine in aqueous solution furnish the corresponding salt of dibromoanthrarufindisulphonic and dibromochrysazindisulphonic acids, which have respectively the formulæ :



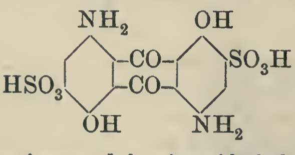
and



These products are yellow, crystalline salts moderately soluble in water. G. T. M.

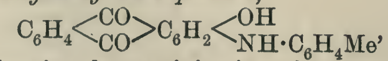
Preparation of Phenanthroanthraquinone. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 194328).—*Phenanthroanthraquinone*, yellow needles, m. p. 234°, is obtained by heating equal parts of phenanthrylbenzoyl-*o*-carboxylic acid and phosphoric oxide at 150° until the product is no longer soluble in aqueous alkalis. The crude quinone is dissolved in the form of its dihydro-derivative by alkaline hyposulphite and re-precipitated from this solution by aerial oxidation. G. T. M.

Preparation of Diaminoanthrarufindisulphonic Acid. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 195139).—*Diaminoanthrarufindisulphonic acid*, blue needles, is readily obtained by stirring together sodium *p*-dibromoanthrarufindisulphonate, aqueous ammonia (20%), and a small amount of copper powder at 30—40°. Other halogenated anthraquinonesulphonic acids behave in a similar manner. G. T. M.



Condensation of Quinizarin with Aromatic Amines. Eugène Grandmougin (*Chem. Zentr.*, 1908, i, 2178—2179 ; from *Rev. Gén. Mat. color*, 1908, 12, 37—39).—Quinizarin is readily reduced to *leucoquinizarin* by moistening it with alcohol, dissolving in very dilute sodium hydroxide solution, and treating with sodium hydrogen sulphite at the boiling temperature. It crystallises in yellow to orange needles, m. p. 155°.

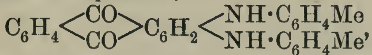
1 : *o-Toluidino-4-hydroxyanthraquinone*,



$$C_6H_4<^{CO}_{CO}>C_6H_2<^{OH}_{NH\cdot C_6H_4Me},$$

is prepared by heating leucoquinizarin with *o*-toluidine and acetic acid to 120—125°; dark violet crystals, m. p. 166°. The *acetate* is a violet-black, crystalline substance, m. p. 149°.

1 : 4-*Di*-o-*toluidinoanthraquinone*,



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C_6H_2}<\begin{matrix}\mathrm{NH\cdot C_6H_4Me}\\\mathrm{NH\cdot C_6H_4Me}\end{matrix},$$

is obtained by heating leucoquinizarin with *o*-toluidine, acetic acid, and anhydrous boric acid; it crystallises in small, dark brown needles, m. p. 223°. The *di*-m-*toluidine* derivative of quinizarin, prepared in a similar manner, crystallises in small, dark blue needles, m. p. 183°, and the *di-diethyl*-p-*phenylenediamine* derivative, $C_{34}H_{36}O_2N_4$, nearly black needles, m. p. 234—235°. The *mono*-p-*toluidine* derivative is violet-black, m. p. 183°; *di*-p-*toluidine* derivative, m. p. 218°.

J. V. E.

Preparation of Alkyl Camphorates. J. D. Riedel (D.R.-P. 196152. Compare this vol., i, 352).—Inactive camphoric acid, like its dextrorotatory constituent, reacts in alkaline solution either with methyl sulphate or the alkyl arylsulphonates to furnish its normal esters. *Methyl* dl-*camphorate*, colourless oil, D 1·073/22°, and b. p. 145—147°/20 mm., is thus obtained by adding alternately potassium hydroxide and methyl sulphate to an aqueous solution of potassium *dl*-camphorate.

G. T. M.

Preparation of *iso*Bornyl Esters of the Fatty Acids from Pinene Hydrochloride or Hydrobromide. Chemische Fabrik von Heyden Akt.-Ges. (D.R.-P. 196017. Compare this vol., i, 351). —*iso*Bornyl esters of the fatty acids are produced by heating together pinene hydrochloride or hydrobromide, the requisite mineral acid, and a zinc salt of some acid, other than a halide or an oxidising agent. Thus *iso*bornyl formate is derived from pinene hydrochloride, formic acid, and anhydrous zinc sulphate. *iso*Bornyl acetate is produced by the interaction of pinene hydrochloride, acetic acid, and zinc *p*-toluenesulphonate.

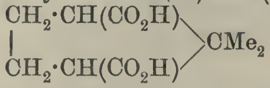
G. T. M.

Preparation of the *iso*Bornyl Esters of Fatty Acids from Pinene Hydrochloride or Hydrobromide. Chemische Fabrik von Heyden Akt.-Ges. (D.R.-P. 194767. Compare this vol., i, 351). —Although zinc chloride and other metallic salts, such as cobalt or cuprous chloride, when heated separately with pinene hydrochloride and glacial acetic acid, give rise only to small yields of *iso*bornyl acetate, yet when a mixture of the zinc salt and that of another heavy metal is employed, a good yield of the required ester is obtained.

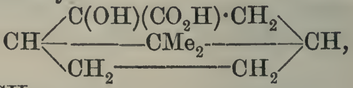
Thus good yields of *iso*bornyl acetate are obtained by boiling a mixture of pinene hydrochloride, glacial acetic acid, and zinc chloride with cuprous, cupric, ferrous, aluminium, cadmium, cobalt, or nickel chloride. *iso*Bornyl formate results in a similar manner from pinene hydrochloride, formic acid, manganous chloride, and zinc chloride.

G. T. M.

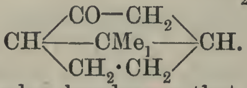
Terpenes and Ethereal Oils. XCIV. The Fenchone Series. Otto Wallach [with Paul Vivck] (*Annalen*, 1908, 362, 174—200. Compare Wallach, this vol., i, 429; Abstr., 1898, i, 486; 1899, i, 65; 1901, i, 331; 1907, i, 541).—The oxidation of *dl*-fenchene by an aqueous alkaline solution of potassium permanganate has been re-investigated, and the results obtained previously (Abstr., 1899, i, 65) confirmed. The hydrocarbon is exceedingly stable towards this oxidising agent, yielding *dl*-hydroxyfenchenic acid, m. p. 154°, and *apo*camphoric acid. *dl*-Hydroxyfenchenic acid is oxidised by lead peroxide and sulphuric acid to fenchocamphorone, which latter is converted by alkaline potassium permanganate into *apo*camphoric acid. Assuming *apo*camphoric acid to have the generally accepted formula (I), then *dl*-hydroxyfenchenic acid and fenchocamphorone must be represented by formulæ (II) and (III) respectively:

(I.) 

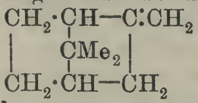
$$\left.\begin{matrix} CH_2\cdot CH(CO_2H) \\ | \\ CH_2\cdot CH(CO_2H) \end{matrix}\right> CMe_2$$

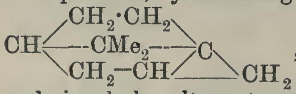
(II.) 

$$CH\left<\begin{matrix} C(OH)(CO_2H)\cdot CH_2 \\ ——CMe_2—— \\ CH_2————CH_2 \end{matrix}\right>CH,$$

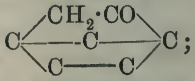
(III.) 

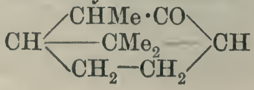
$$CH\left<\begin{matrix} CO—CH_2 \\ —CMe_2— \\ CH_2\cdot CH_2 \end{matrix}\right>CH.$$

The conclusion might also be drawn that *dl*-fenchene has the structural formula  $$\begin{matrix} CH_2\cdot CH—C\colon CH_2 \\ | \quad CMe_2 \quad | \\ CH_2\cdot CH—CH_2 \end{matrix}$$, but the great stability of the hydrocarbon towards permanganate is not in agreement with this formula.

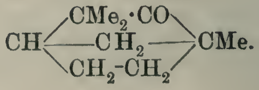
The *dl*-fenchene used in this investigation was obtained by adding sodium nitrite and acetic acid to an aqueous solution of fenchylamine hydrochloride. An oil, b. p. 175—178°, was obtained together with the fenchene, and was found on investigation to be a mixture of *d*-limonene, cineole, and dipentene; the latter substance was probably formed as a secondary product from either the *d*-limonene or cineole. It is possible, by assuming *dl*-fenchene to have the structural formula  $$CH\left<\begin{matrix} CH_2\cdot CH_2 \\ —CMe_2— \\ CH_2—CH \end{matrix}\right>C\left<\begin{matrix} \\ CH_2 \end{matrix}\right.$$, to represent the formation of *d*-limonene and cineole by alternate processes of hydrolysis and dehydration.

The "*iso*fenchene" obtained by Bertram and Helle (Abstr., 1900, i, 398) from *iso*fenchyl alcohol is shown to be identical with *dd*-fenchene obtained from fenchyl alcohol (compare Wallach, Abstr., 1899, i, 65).

*iso*Fenchone, derived from *iso*fenchyl alcohol, is oxidised by permanganate to an acid, $C_{10}H_{16}O_4$, which, since it is isomeric with camphoric acid, is named *iso*fenchocamphoric acid. It is therefore evident that *iso*fenchone must contain the grouping  $$C\left<\begin{matrix} CH_2\cdot CO \\ —C— \\ C——C \end{matrix}\right>C;$$ further, since fenchone and *iso*fenchone behave so differently on oxidation, they must have widely different constitutions. Neither the author's fenchone formula (I) nor Semmler's formula (II) is to be regarded as firmly established:

(I.) 

$$CH\left<\begin{matrix} CHMe\cdot CO \\ —CMe_2— \\ CH_2—CH_2 \end{matrix}\right>CH$$

(II.) 

$$CH\left<\begin{matrix} CMe_2\cdot CO \\ —CH_2— \\ CH_2\text{-}CH_2 \end{matrix}\right>CMe.$$

dl-Fenchene, prepared from fenchylamine, is the purest as yet obtained; it has b. p. 156—157°, D_{19} 0·869, n_D^{19} 1·4724, and α_D^{18} $-32·2°$ (in 1-dcm. tube). The *dibromide*, $C_{10}H_{16}Br_2$, prepared by acting on the hydrocarbon with bromine in acetic acid, forms colourless crystals, m. p. 87—88°, $[\alpha]_D^{11}$ $+42·83°$ (in ethyl acetate).

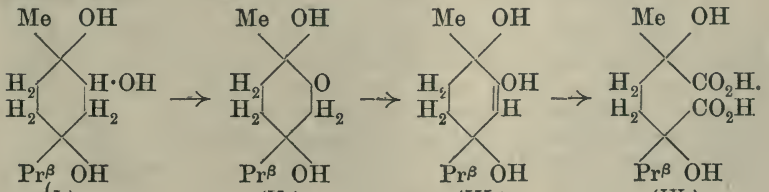
dl-Hydroxyfenchenic acid is now found to have m. p. 154°, $[\alpha]_D^{13}$ $-62·98°$ (in ether).

*iso*Fenchone readily forms a *semicarbazone*, $C_{11}H_{19}ON_3$, which crystallises in needles, m. p. 221—222°, $[\alpha]_D^{11}$ $-8·27°$ (in methyl alcohol). *Bromo*iso*fenchone*, $C_{10}H_{15}OBr$, is readily formed by the action of bromine on *iso*fenchone at the ordinary temperature; it forms colourless crystals, m. p. 56—57°, $[\alpha]_D^{15}$ $-164·1°$ (in ethyl alcohol).

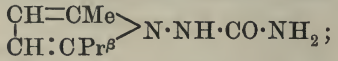
iso*Fenchocamphoric acid*, $C_{10}H_{16}O_4$, obtained by oxidising *iso*fenchone or *iso*fenchyl alcohol with an aqueous alkaline solution of potassium permanganate, has m. p. 158—159°, $[\alpha]_D^{11}$ $-12·75°$ (in ether); the *silver* salt, $C_{10}H_{14}O_4Ag_2$, was prepared and analysed.

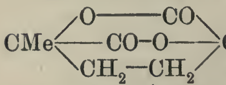
The following derivatives of *l*-fenchone were prepared; they melt at the same temperatures as the corresponding *d*-fenchone derivatives; the values in brackets are the m. p.'s of the racemic compounds: iso*fenchyl phenylcarbamate*, m. p. 107° (94°); iso*fenchone semicarbazone*, m. p. 221—222° (223—224°); iso*fenchoneoxime*, m. p. 82° (133°); *bromo*iso*fenchone*, m. p. 56—57° (46—47°); iso*fenchocamphoric acid*, m. p. 158—159° (174—175°). W. H. G.

Terpenes and Ethereal Oils. XCV. Alcohols of the Terpinene Series (Terpinenols). OTTO WALLACH (*Annalen*, 1908, **362**, 261—284. Compare this vol., i, 429).—I. *Degradation Products of Terpinene-4-ol* (Δ^1-*Menthene-4-ol*). [With FRITZ MEISTER.]—It was shown previously (Abstr., 1907, i, 943) that, on oxidation with alkaline permanganate, trihydroxyterpane yields an optically active acid, m. p. 205—206°, and an optically inactive isomeric acid. m. p. 188—189°. It is found now that, when heated with permanganate and dilute sulphuric acid at 60—70°, both acids yield dimethylacetonylacetone, and must therefore have the constitution (IV). The oxidation of the trihydroxyterpane (I) is considered to lead in the first place to the formation of a dihydroxyketone (II), which changes in the alkaline solution into the enolic form (III), and then undergoes further oxidation with resolution of the ring between the carbon atoms 2 and 3. Such a reaction may take place also in other cases, and may explain the difference in the oxidation products sometimes obtained on resolution of cyclic compounds with permanganate and with chromic acid:



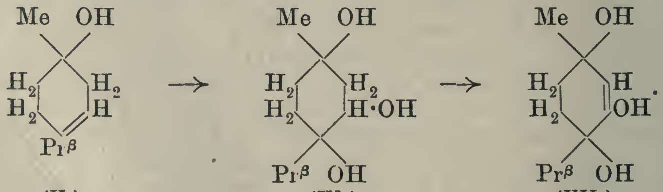
(I.) (II.) (III.) (IV.)

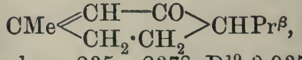
The semicarbazone of dimethylacetonylacetone (Posner, Abstr., 1902, i, 82) is considered to have the constitution  $\begin{matrix}CH{=}CMe \\ CH{:}CPr^{\beta}\end{matrix}{>}N{\cdot}NH{\cdot}CO{\cdot}NH_2$; it does not yield the ketone when heated with 10% sulphuric acid, is resinified by boiling with strong acids, and when heated alone evolves vapours giving the pyrolle reaction.

The dilactones of the isomeric acids must have the constitution , and are formed from two six-atom, heterocyclic nuclei (compare Le Sueur, Trans., 1907, **93**, 716).

II. *Synthesis of* $\alpha\alpha'$*-Dihydroxy-*α*-methyl-*α'-iso*propyladipic Acid.* [With Fritz Meister.]—With the object of confirming the constitution ascribed to the isomeric acids obtained by oxidation of trihydroxyterpane, dimethylacetonylacetone was treated with potassium cyanide and hydrochloric acid at 0°, and subsequently on the water-bath; on distillation with steam, the product yielded the dilactone, m. p. 72—73°, which on hydrolysis with boiling alkali was converted into the optically inactive acid, m. p. 188—189°.

III. *Terpinene-*1*-ol* [Δ^3-p-*Menthene*-1-*ol*] *and its Degradation Products.* [With Fritz Meister.]—The unsaturated alcohol, $C_{10}H_{17}{\cdot}OH$, b. p. 208—210°, obtained from the fractions of commercial terpineol boiling at low temperatures cannot be, as was thought (*loc. cit.*), identical with terpinene-4-ol, as the trihydroxyterpane, m. p. 120°, obtained from it yields when heated with acids, not carvenone, but a ketone with an odour of menthone. The alcohol is now considered to be terpinene-1-ol (V). This, on oxidation, must yield 1 : 3 : 4-trihydroxyterpane (VI), which, on further oxidation, should be converted by way of the enolic form (VII) into $\alpha\alpha'$-dihydroxy-α-methyl-α'-*iso*propyladipic acid (IV). The identity of the acid thus obtained has been confirmed by its conversion into the dilactone, m. p. 72°, and into dimethylacetonylacetone.

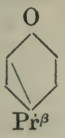

(V.) (VI.) (VII.)

The *ketone* (Δ^1-*menthenone*),  $CMe{<}\begin{matrix}CH{-}CO \\ CH_2{\cdot}CH_2\end{matrix}{>}CHPr^{\beta}$, formed from 1 : 3 : 4-trihydroxyterpane, has b. p. 235—237°, D^{19} 0·9375, n_D^{19} 1·4875, and forms a sparingly soluble *semicarbazone*, m. p. 224—226°, which yields the ketone again when heated with sulphuric acid. When treated with sodium in ethereal solution, the ketone yields a *pinacone* and an *alcohol*, which is oxidised by chromic acid, forming *i*-menthone. The semicarbazone of this has m. p. 210—212°. A comparison of the physical properties of Δ^1-menthenone with those of carvenone, carvotanacetone, Δ^4-menthenone, and Callenbach's menthenone (see Rabe and Rahm, Abstr., 1904, i, 757; Merling, Abstr., 1905, i, 349), shows that the new ketone most closely resembles carvenone.

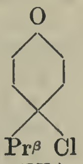
Δ^4-Menthenone, purified by conversion into its oxime and liberation by means of sulphuric acid, has b. p. 213°, D^{21} 0·918, n_D^{21} 1·4720; the semicarbazone has m. p. 142°; the *dibromide*, $C_{10}H_{16}OBr_2$, m. p. 36°. On reduction, menthenone yields a mixture of stereoisomeric menthols, including *i*-menthol, which forms a semicarbazone, m. p. 212°.

IV. *Synthesis of the Two Tertiary Alcohols of the Terpinene Series, Terpinene-*4*-ol* (Δ^1*-Menthene-*4*-ol*) *and Terpinene-*1*-ol* (Δ^3*-Menthene-*1*-ol*).—The formation of terpinene-4-ol from sabinene hydrate was described previously (this vol., i, 430). The crystalline sabinene hydrate, formed by the action of magnesium methyl iodide on sabina ketone, has $[\alpha]_D$ +53·67°, and when shaken with sulphuric acid yields terpinene-4-ol, which has $[\alpha]_D$ +10·53°, and is identical with the terpinenol from cardamom and majorana oils, but may contain small amounts of the inactive alcohol.

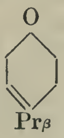
[With Richard Heyer.]—Terpinene-1-ol (XI) is prepared from sabinaketone (VIII) by conversion of this by way of its hydrochloride (IX) into Δ^3-*iso*propylhexenone (X) and treatment of the product with magnesium methyl iodide. Δ^3-*iso*Propylhexenone has b. p. 95—96°/12 mm., D^{22} 0·944, n_D^{22} 1·4817. Terpinene-1-ol has b. p. 92—97°/14 mm., D^{24} 0·9210, n_D^{24} 1·4778, and loses water when distilled under the ordinary pressure, forming phellandrene. The ethylene linking undergoes transmigration during the decomposition of the terpinenol, or Δ^3-*iso*propylhexenone isomerises to Δ^2-*iso*propylhexenone during the Grignard reaction, in which case the resulting alcohol must be phellandrene hydrate (XII). As on oxidation the synthetic alcohol yields 1 : 3 : 4-trihydroxyterpane, it must contain at least considerable quantities of terpinene-1-ol.



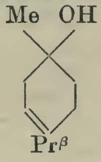
(VIII.)



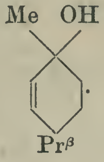
(IX.)



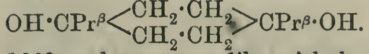
(X.)



(XI.)

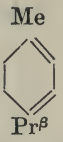


(XII.)

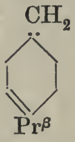
V. *Other Syntheses in the Terpinene Group.*—The action of magnesium *iso*propyl iodide on sabina ketone leads to the formation of a tertiary *alcohol*, which is obtained as a viscid oil, b. p. 102—107°/14 mm., and, when shaken with dilute sulphuric acid, slowly forms the *terpin*,  $OH{\cdot}CPr^{\beta}\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\!>\!CPr^{\beta}{\cdot}OH$. This crystallises in plates, m. p. 139°, and reacts readily with hydrogen haloids in glacial acetic acid solution. The *dichloride*, $C_{12}H_{22}Cl_2$, has m. p. 111—112°; the *dibromide*, m. p. 120—121°. G. Y.

Terpenes and Ethereal Oils. XCVI. Terpinene and its Modifications. Otto Wallach (*Annalen*, 1908, 362, 285—304).—I. *β-Terpinene.*—β-Terpinene (Abstr., 1907, i, 1058) is now found to have b. p. 173—174°, D^{22} 0·838—0·840, n_D^{22} 1·4751—1·4754. With bromine in alcoholic-ethereal solution, it forms a sparingly soluble *tetrabromide*, $C_{10}H_{16}Br_4$, crystallising in prisms, m. p. 154—155°, and when treated with water and oxygen in presence of sunlight is converted into dihydrocuminaldehyde, which is further oxidised to cuminaldehyde. Oxidation of β-terpinene with permanganate in aqueous solution leads to the formation of a neutral *product*, which distils at 225°/10 mm., yielding small amounts of a crystalline *substance*, and when treated with dilute sulphuric acid, without previous distillation, yields an oil having a strong odour of cuminaldehyde and forming a *semicarbazone*, m. p. 201—202°.

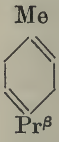
II. *Constitution of Ordinary Terpinene.*—It has been shown previously (Abstr., 1907, i, 943) that terpinene must be one of, or a mixture of two or three of, the three substances having the annexed formulæ. These three substances yield the same dihydrohaloids.



α-Terpinene

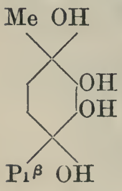


β-Terpinene



γ-Terpinene

Terpinene has now been obtained (*a*) from the dihydrochloride, m. p. 52°, (*b*) by inversion of pinene, and (*c*) synthetically from sabinaketone. Ordinary terpinene, b. p. 179—181°, cannot contain β-terpinene, as this has now been found to boil at a lower temperature than limonene, to form terpinene nitrosite only slowly and incompletely, and to yield oxidation products; moreover, ordinary terpinene does not form a crystalline tetrabromide. α-Terpinene, on oxidation with permanganate, must form 1:2:3:4-tetrahydroxyterpane (erythritol), which, on further oxidation, yields αα′-dihydroxy-α-methyl-α′-*iso*propyladipic acid (see preceding abstract). It is found, however, that, on oxidation with permanganate, ordinary terpinene, prepared by method (*a*), (*b*), or (*c*), yields in addition to this acid an erythritol, m. p. 236—237°, which does not form the dihydroxyadipic acid on further oxidation; ordinary terpinene must therefore be a mixture of hydrocarbons, α-terpinene being the chief component. The other hydrocarbon present can be either γ-terpinene or terpinolene, and the latter on oxidation does not yield the erythritol, m. p. 236—237°. It is held that terpinene nitrosite is derived from α-terpinene.



G. Y.

Philippine Terpenes and Essential Oils. I. Raymond F. Bacon (*Philippine J. Sci.*, 1908, 3, 49—64).—When a mixture of limonene hydrochloride and ether is treated with magnesium and the product decomposed with cold dilute sulphuric acid, a hydrocarbon, $C_{10}H_{18}$, b. p. 174—176°, is produced, which has D_4^{30} 0·8257, n_D^{30} 1·4585, and $[\alpha]_D^{30}$ 90·3°, and is probably identical with the dihydrolimonene obtained by Semmler (Abstr., 1903, i, 505) by the reduction of limonene hydrochloride with sodium and alcohol. The hydrochloride of this compound was prepared and submitted to the Grignard reaction, when a *hydrocarbon*, $C_{10}H_{20}$, b. p. 171—174°, was obtained, which has D_4^{30} 0·8052, n_D^{30} 1·4459, and $[\alpha]_D^{30}$ 3·7°. When benzaldehyde is added to the product of the action of magnesium on limonene hydrochloride, the hydrocarbon, $C_{10}H_{18}$, is liberated, and a *compound*, $C_6H_5{\cdot}COMgCl$, is produced, which is decomposed by dilute acids with formation of benzaldehyde, and is converted by heat into benzoin and other substances. Acetone reacts with the magnesium compound in a similar way.

When magnesium benzyl chlorid is treated with benzaldehyde, phenylbenzylcarbinol, m. p. 67—68°, is produced. E. G.

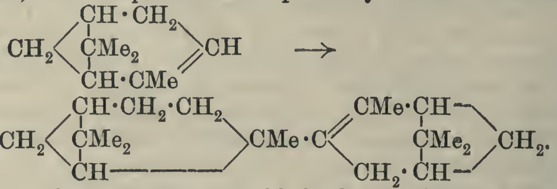
Philippine Terpenes and Essential Oils. II. Ylang-ylang Oil. RAYMOND F. BACON (*Philippine J. Sci.*, 1908, 3, 65—86).—Determinations have been made of the sp. gr., rotatory power, refractive index, and ester number of samples of Philippine ylang-ylang oil of different grades and origin. The ester number of first-grade oils is usually about 100, whilst that of second-grade oils rarely exceeds 80. The refractive index of the former is rarely more than 1·4900, whereas that of the latter approaches 1·5000. This difference is due to the fact that the second-grade oils contain more sesquiterpenes and resins. For the same reason, $[\alpha]_D$ of the first-grade oils is usually below $-45°$, whilst that of the second-grade is $-60°$ or more.

A study of the composition of the oil has confirmed, on the whole, the work of previous observers, and has shown that the following substances are present: esters of formic, acetic, valeric (?), benzoic, and salicylic acids; methyl and benzyl alcohols; pinene, cadinene, and other terpenes and sesquiterpenes; linalool, geraniol, and safrole; eugenol, *iso*eugenol, and *p*-cresol, probably as methyl ethers; and creosol.

The following esters have been prepared for comparison: *benzyl salicylate*, b. p. 186—188°/10 mm.; benzyl benzoate, b. p. 315—320°; *benzyl methyl ether*, b. p. 166—168°; *benzyl formate*, b. p. 84—85°/10 mm.; *geranyl methyl ether*, b. p. 100—105°/10 mm. and 208—212°/760 mm.; *linalyl methyl ether*, b. p. 189—192°, and *geranyl benzoate*, b. p. 198—200°/15 mm. E. G.

Method of Obtaining Resins from Turpentine and the Preparation from them of Lacs, Varnishes, &c. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 800—805).—This method consists in treating turpentine oil with sulphuric acid of 66° B. and formaldehyde, neutralising with ammonia, separating the ammonium sulphate, and heating with ammonia. After drying at 70—80°, a yellowish-brown resin is obtained, which is soluble in alcohol, benzene, toluene, ether, or acetic acid, giving yellow solutions. It also dissolves in solvent naphtha or ethyl acetate, and the solutions in these solvents form quick-drying, elastic lacs.

The chemical constituents of the lacs obtained were not determined, but it is probable that they consist of a hydrocarbon, or mixture of hydrocarbons, produced by a series of condensations. For example, with pinene, the sulphuric acid probably causes condensation in two stages



Continuation of this process would lead to still more complicated hydrocarbons. The formaldehyde probably reacts with the mobile hydrogen atoms, giving $\cdot CH_2\cdot OH$ groups. The alcohols so formed would lose water on heating, giving rise to methylene derivatives of terpenes and polyterpenes. T. H. P.

Resins from Conifers, and Treatment of the Resinous Sap from Pinus maritima, P. sylvestris, and other Species. W. Schkateloff (*Chem. Zentr.*, 1908, i, 2097—2100; from *Moniteur scient.*, 1908, [4], 22, 217—227. Compare Abstr., 1907, i, 213).—From studying the composition of the resin from *Pinus sylvestris*, the author comes to the conclusion that in all ordinary resins, such as colophony, galipot, resinous saps, &c., the same resin acid is present in the following isomeric modifications: (1) *α-Sylvic acid*, a white, crystalline powder, m. p. 143—144°, $[\alpha]_D - 73{\cdot}67°$; (2) *β-sylvic acid*, crystallising in three-sided plates, m. p. 160°, $[\alpha]_D - 92{\cdot}5°$; (3) *γ-sylvic acid*, crystallising in long needles or three-sided plates, m. p. 179—180°, optically inactive. Of these modifications, β-sylvic acid appears to be identical with the abietic acid described by Mach and Levy, and γ-sylvic acid identical with pyromaric acid described by Laurents. A yellow, acid, uncrystallisable resin, called by Unverdorben pinic acid, was found accompanying these three isomeric acids in all crude products. It is produced from the isomeric resin acids by oxidation when exposed to the air. The evidence so far obtained indicates that the formula of the resin acids may be $C_{20}H_{28}O_2,\frac{1}{2}H_2O$, an unsaturated compound containing two double linkings. Considerable contradiction and confusion as to the properties of these resin acids is caused by the difficulty of investigating them. As an instance of this, it is stated that if α-sylvic acid from *P. sylvestris* is melted, a pale colophony is obtained, $[\alpha]_D - 73{\cdot}5°$; the same acid from *P. abies excelsa* gives a colophony, $[\alpha]_D - 74{\cdot}1°$, which, if heated in an air-oven to 170°, shows $[\alpha]_D - 60°$, and $[\alpha]_D - 18°$ after heating to 180—190°, finally becoming inactive.

The Properties of Resinous Saps from Various Pines.—(*a*) From *Pinus sylvestris*: gives, when steam-distilled, 15—16% turpentine oil, $[\alpha]_D + 22°$ to $+ 24°$, or rectified over sodium hydroxide, $[\alpha]_D + 25{\cdot}1°$, D^{15} 0·867. The acid present in the sap is α-sylvic acid. (*b*) From *P. abies excelsa*: gives very little resin; the resin sap contains about 13·4% oil, D^{15} 0·873, $[\alpha]_D - 13{\cdot}2°$, and also α-sylvic acid, m. p. 143° and $[\alpha]_D - 74{\cdot}1°$. (*c*) *Larix sibirica* gives very little resin sap, 14·13% oil of D^{19} 0·870, $[\alpha]_D - 14{\cdot}3°$, and β-sylvic acid. (*d*) *Pinus cembra* gives only 6% oil of D^{15} 0·865, $[\alpha]_D + 14{\cdot}04°$; another portion contained 20% oil of b. p. 155—156° and $[\alpha]_D$ +17°, and from the solid resin, β-sylvic acid was obtained. (*e*) *P. taurica* gave a quantity of the same resin as *P. maritima*; the resinous sap contained 20% oil of D^{19} 0·861 and $[\alpha]_D$ −75·9°, and the solid resin, α-sylvic acid. (*f*) *Abies sibirica*: the resin sap is a very aromatic, clear liquid containing 28% oil, D^{19} 0·8751, $[\alpha]_D$ −35·6°, but no crystallisable substance. (*g*) *Pinus strobus*: the resin sap is similar to that of ordinary pine, and contains α-sylvic acid. J. V. E.

Decomposition of Amygdalin by Emulsin. Leopold Rosenthaler (*Arch. Pharm.*, 1908, **246**, 365—366).—Feist (this vol., i, 437) regards *d*-benzaldehydecyanohydrin, formed when emulsin acts on amygdalin, as a primary product in the hydrolysis. The author, however, has now shown experimentally that *d*-benzaldehydecyanohydrin is formed from benzaldehyde and hydrocyanic acid by emulsin, and is therefore a secondary synthetic product. G. B.

Constitution of Vicianin. I. Gabriel Bertrand and Gustave Weisweiller (*Compt. rend.*, 1908, **147**, 252—254).—Vicianin (Abstr., 1907, i, 68), like amygdalin and Dakin's *iso*amygdalin (Trans., 1904, **85**, 1512), when dissolved in concentrated sulphuric acid gives a carmin-red coloration, slowly whilst cold, rapidly on heating. Schiff (Abstr., 1900, i, 49) considered this reaction as characteristic of mandelonitrile. The presence of the group ·O·CHPh·CN in vicianin is proved by two reactions: (1) When an aqueous solution of the crystallised glucoside is treated at 35° with an extract of the seeds of *Vicia angustifolia*, hydrogen cyanide (estimated by Denigès' method, Abstr., 1896, ii, 385) and benzaldehyde (estimated by conversion into the phenylhydrazone) are produced in equal molecular quantities. (2) By evaporating to dryness vicianin (4 grams) with fuming hydrochloric acid (25 c.c.), *l*-mandelic acid is produced. The acid obtained has m. p. 132—133° (on Maquenne block) and $[\alpha]_D$ −153·3° (at 18° and 1% solution), whilst Walden (Abstr., 1896, ii, 137) found m. p. 131—132° and $[\alpha]_D$ −133·06°. The conclusion is drawn that vicianin, like amygdalin, is a derivative of *l*-mandelonitrile. E. H.

Action of Hydrochloric Acid on Santonin and its Derivatives. Mechanism of the Formation of Desmotroposantonin. Luigi Francesconi and G. Cusmano (*Gazzetta*, 1908, **38**, ii, 101—110).—It has been stated by Wedekind (*Chem. Zeit.*, 1902, No. 13), and by Wedekind and Schmidt (*Arch. Pharm.*, 1906, **244**, 623), that santonic acid is transformed into desmotroposantonin by the action of hydrochloric acid. The authors show that no such change takes place, and that the method of preparation of santonic acid probably employed by Wedekind (Abstr., 1898, i, 596) gives mixtures of santonic acid with santoninic acid or santonin, which mixtures have, in some cases, a melting point practically the same as that given by Wedekind, and cannot be freed from impurity by crystallisation from a mixture of alcohol and ether.

Santonic acid and desmotroposantonin are not acted on by dry hydrogen chloride. When cooled with a mixture of ice and salt, santonin absorbs 2 mols. of hydrogen chloride, one of which is eliminated rapidly at the ordinary temperature in an atmosphere of hydrogen chloride, and the other, slowly in presence of an extraneous gas. Both these hydrochlorides yield santonin when treated with water or sodium hydroxide, and are related to santonin in the same way as the coloured, unstable additive products of ketones with the halogen hydracids are related to the ketones themselves (compare this vol., i, 801). Both these hydrochlorides change gradually into a monohydrochloride, which is not capable of absorbing hydrogen chloride, and yields desmotroposantonin by the action of water or by spontaneous elimination of hydrogen chloride. The formation of these different hydrochlorides and that of desmotroposantonin from them are explained in the same way as the formation of the various hydrochlorides of the unsaturated, aromatic ketones (*loc. cit.*).

T. H. P.

Sapotoxin and Sapogenin from Agrostemma githago. II. J. Brandl (*Arch. exp. Path. Pharm.*, 1908, **59**, 245—268).—A second sapotoxin can be obtained from the lead acetate precipitate from the crude sapotoxin, which can be purified by precipitation by ethyl alcohol from the solution in methyl alcohol. It is designated *agrostemmic acid.* It has a considerably higher molecular weight than the *A*-sapotoxin. It yields on hydrolysis sapogenin, $C_{35}H_{54}O_{10}$, in a yield of 38%, and sugars, calculated as dextrose, in a yield of 50·67%. The sugars obtained by the hydrolysis of the saponins consist of dextrose and galactose, with possibly some arabinose.

The potassium salt of sapogenin methyl ester, when pure, has a composition corresponding with $C_{36}H_{55}O_{10}K$. By treating the potassium salt or its methyl esters with methyl sulphate, a series of methyl derivatives can be obtained, the yield of which varies with the conditions of experiment. The monomethyl derivative, which is crystalline, but has no definite m. p., corresponds with the formula $C_{36}H_{56}O_{10}$. The higher methyl derivatives are not crystalline.

By heating sapogenin with potassium hydroxide at 160—175°, an acid, $C_{30}H_{46}O_4$, is obtained, which does not melt at 290°, and yields a dimethyl ester, m. p. 231—232°. This acid is also obtained from dogs' fæces after ingestion of sapotoxin.

The toxic effects of the seeds of *Agrostemma githago*, of agrostemmic acid, and of the sapotoxin are similar. The seeds in quantities of 10 grams per kilo. in pigeons, and 15 grams per kilo. in hens, ingested *per os* cause death in two to three days. Vomiting, diarrhœa, salivary flow, and paralysis are the chief symptoms.

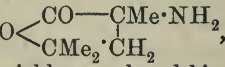
S. B. S.

Sweet Substances from Eupatorium Rebaudianum and Liquorice. Paul Rasenack (*Chem. Zentr.*, 1908, ii, 78—79; from *Arb. Kais. Gesundh.-Amt.*, 1908, **28**, 420—443).—The sweet material which is contained chiefly in the leaves of *Eupatorium Rebaudianum* was obtained by extracting with alcohol and then precipitating with ether. The crude product separates from methyl alcohol in slender, white needles, which shrink at 180—190°, m. p. 200—210° (decomp.). The composition of this substance appears to be $C_{42}H_{72}O_{21}$, and its behaviour towards salt solutions differs from that of glycyrrhizin.

When boiled with dilute sulphuric acid, it gives dextrose and a tasteless substance, forming small, prismatic crystals, m. p. 226—227°, which are sparingly soluble in water, and appear to have the composition $C_{30}H_{40}O_5$. The author has investigated the sweet material from liquorice root, and detected the presence of saccharose therein. From the results of analysis, the formula for glycyrrhizic acid is considered to be $C_{44}H_{60}O_{18}$. J. V. E.

Aminolactones from Diacetone Alcohol. Moritz Kohn (*Monatsh.*, 1908, **29**, 509—518. Compare this vol., i, 829).—The use of diacetone alcohol (*β*-methylpentane-*β*-ol-*δ*-one) instead of diacetoneamine in the Bucherer and Zelinsky reaction (*loc. cit.*) leads in a similar manner to the formation of tetrahydrofuran derivatives in place of those of pyrrolidone.

4-*Amino-5-keto-2 : 2 : 4-trimethyltetrahydrofuran*,



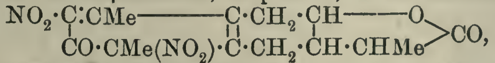
$$O<\begin{array}{l}CO—CMe\cdot NH_2\\ CMe_2\cdot CH_2\end{array},$$

m. p. 30—34°, b. p. 122—124°/14—16 mm., yields a *phenylthiocarbamide*, m. p. 195—198°. 4-*Methylamino-5-keto-2 : 2 : 4-trimethyltetrahydrofuran*, $C_8H_{15}O_2N$, b. p. 108—111°/12 mm., forms a *phenylthiocarbamide*, m. p. 152—154°.

The reaction between the alcohol, potassium cyanide, and dimethylamine hydrochloride leads to the ultimate formation of a liquid, b. p. 113°/12 mm., which is a mixture of Franke and Kohn's 4-hydroxy-5-keto-2 : 2 : 4-trimethyltetrahydrofuran (Abstr., 1907, i, 816) and 4-*dimethylamino-5-keto-2 : 2 : 4-trimethyltetrahydrofuran*, $C_9H_{17}O_2N$, of which the *platinichloride*, and the *methiodide* with its *aurichloride* and *platinichloride* are mentioned. C. S.

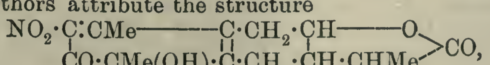
Action of Nitric Acid on Desmotroposantonin. Guido Bargellini and V. Daconto (*Gazzetta*, 1908, **38**, ii, 41—52. Compare Abstr., 1907, i, 931).—When oxidised by means of chromic acid, desmotroposantonin yields a compound which, with phenylhydrazine in dilute acetic acid, gives an insoluble, red product, but the amount obtained was too small to admit of its further study.

On treating desmotroposantonin with nitric acid under the conditions given by Andreocci (Abstr., 1898, i, 266), the authors find that the first compound formed is not the nitrodesmotroposantonin described by Andreocci, but a nitroquinitrole, m. p. 120°, of the constitution



$$\begin{array}{l}NO_2\cdot C{:}CMe———C\cdot CH_2\cdot CH——O\\ CO\cdot CMe(NO_2)\cdot C\cdot CH_2\cdot CH\cdot CHMe\end{array}>CO,$$

which decomposes readily into one or other of the three compounds described by Andreocci (*loc. cit.*), according to the conditions. To the compound, m. p. 240°, obtained by Andreocci by the action of hot dilute nitric acid or cold concentrated nitric acid on desmotroposantonin, the authors attribute the structure



$$\begin{array}{l}NO_2\cdot C{:}CMe———C\cdot CH_2\cdot CH——O\\ CO\cdot CMe(OH)\cdot C\cdot CH_2\cdot CH\cdot CHMe\end{array}>CO,$$

which is more in accord with its mode of formation from the nitroquinitrole and with its behaviour as a nitroquinol than is the constitution suggested by Andreocci. The authors could not obtain Andreocci's third substance, m. p. 145°, in a pure state.

The *nitroquinitrole*, $C_{15}H_{16}O_7N_2$, obtained as an amorphous, white powder, m. p. about 120° (decomp.), like all quinitroles, decomposes readily with evolution of oxides of nitrogen. When decomposed by means of methyl or ethyl alcohol, it gives an almost quantitative yield of nitrodesmotroposantonin, $C_{15}H_{17}O_5N$, which separates from alcohol in trimetric crystals [A. Rosati: $a:b:c=0·4133:1:2·2646$], m. p. 189—190°, $[\alpha]_D^{24}+115·38°$. Nitrodesmotroposantonin exhibits all the characters of the nitrophenols, and yields an *acetyl* derivative,

$C_{17}H_{19}O_6N$,

which crystallises from alcohol in white needles, m. p. 166—167°, $[\alpha]_D^{23}+111·79°$

The nitroquinol, m. p. 237—240° (decomp.), which can also be obtained by heating the nitroquinitrole or nitrodesmotroposantonin on the water-bath with nitric acid (D 1·23), dissolves readily in concentrated sulphuric acid, giving a cherry-red solution, and yields an *acetyl* derivative, $C_{17}H_{19}O_7N$, m. p. 186—188°. When reduced by means of sulphuric acid, the nitroquinol is converted into nitrodesmotroposantonin, whilst reduction by zinc and acetic acid yields a red, amorphous substance, which appears to be analogous to that obtained by Wedekind (Abstr., 1905, i, 134) by reducing benzene azodesmotroposantonin with stannous chloride and hydrochloric acid.

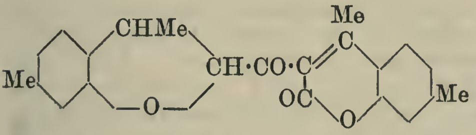
[With A. Mannino.]—*l*-Desmotroposantonin behaves towards nitric acid in the same way as desmotroposantonin, a nitroquinitrole being first formed. The *nitroquinol*, $C_{15}H_{17}O_6N$, crystallises from acetic acid in colourless needles, m. p. 218—220° (decomp.), dissolves in concentrated sulphuric acid, giving a red coloration, and is lævorotatory.

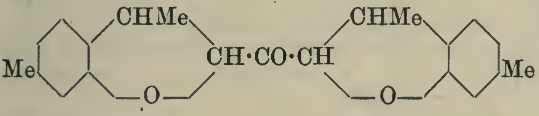
T. H. P.

Conversion of Coumarins into Coumarinic Acids and *o*-Coumaric Acids. Karl Fries and W. Klostermann (*Annalen*, 1908, 362, 1—29).—It has been shown previously (Abstr., 1906, i, 276) that 7-methylcoumarin, 4 : 7-dimethylcoumarin, and 3 : 4 : 7-trimethylcoumarin differ in their behaviour towards aqueous alkalis. The rate of formation of coumarinic acids from these substituted coumarins, and also from 4 : 7-dimethyl-3-ethylcoumarin and 3-benzyl-4 : 7-dimethylcoumarin, on treatment with an aqueous solution of potassium hydroxide has now been measured. It is found that the velocity with which the coumarin is converted into the corresponding coumarinic acid decreases, not only with an increase in the number, but also in the size, of the alkyl or aryl group. This is shown by the following comparative values representing the velocity of formation of the coumarinic acid : 7-methylcoumarin = 150, 4 : 7-dimethylcoumarin = 100, 3 ; 4 : 7-trimethylcoumarin = 75, 4 : 7-dimethyl-3-ethylcoumarin = 45, 3-benzyl-4 : 7-dimethylcoumarin = 35.

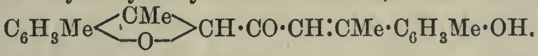
The behaviour of these substituted coumarins on treatment with sodium ethoxide is far more complicated. Ebert has shown (Abstr., 1885, 391) that coumarin and 7-methylcoumarin are converted into the corresponding *o*-coumaric acids when heated with sodium ethoxide. It has now been found possible to isolate the hitherto unknown ethyl esters of these acids, formed as intermediate products during the reaction. The esters themselves are colourless, but their alkali salts are yellow; it is therefore not improbable that the salts have the quinonoid structure $O\colon C_6H_4\colon CH\cdot CH\colon C(OEt)ONa$. This view receives support from the fact that an alcoholic ammoniacal solution of the ester reduces silver nitrate, whereas neither *o*-coumaric acid nor ethyl cinnamate reduces silver nitrate under similar conditions. The yellow, aqueous solutions of these salts are not fluorescent.

4 : 7-Dimethylcoumarin when heated with sodium ethoxide or methoxide is not converted into the corresponding coumaric acid, but yields a ketone which probably has the annexed formula. It is proposed to name the group $C_6H_4 < \substack{CH_2 \\ -O-} > CH\cdot CO-$, hydrocoumarilyl, hence this ketone is 3-[2 : 5-dimethylhydrocoumarilyl]-4 : 7-dimethylcoumarin. It is converted by aqueous alkalis into another ketone, thus: $C_{22}H_{20}O_4 + H_2O \longrightarrow C_{21}H_{22}O_3 + CO_2$. This new compound is probably 1-[2 : 5-dimethylhydrocoumarilyl]-2 : 5-dimethyl hydrocoumarone, having the annexed formula.





The solubility of this substance in alkalis and the formation of a methoxy-derivative on treating a solution in alcoholic sodium ethoxide with methyl iodide may be explained by assuming a transformation into an enolic form, but the compound does not give a coloration with ferric chloride and does not react with copper acetate. It is possible that in the formation of the salts, the hydrocoumarone ring opens, forming an *o*-hydroxybenzylidene derivative,



$$C_6H_3Me < \substack{CMe \\ -O-} > CH\cdot CO\cdot CH\colon CMe\cdot C_6H_3Me\cdot OH.$$

This would account for the yellow colour of the salts, but the fact that the methoxy-derivative is colourless then becomes remarkable.

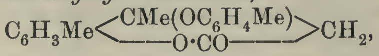
4 : 6-Dimethylcoumarin, like the isomeric 4 : 7-dimethyl compound, is converted by sodium ethoxide into a ketone, $C_{21}H_{22}O_2$, similar to that just described.

3 : 4 : 7-Trimethylcoumarin, 4 : 7-dimethyl-3-ethylcoumarin, and 3-benzyl-4 : 7-dimethylcoumarin are converted by sodium ethoxide into sodium salts of the corresponding coumarinic acids.

The effect of the presence of alkyl groups on the reconversion of coumaric acids into coumarins is very marked; thus β : 4-dimethyl-*o*-coumaric acid and β : 5-dimethyl-*o*-coumaric acid in acetic acid are converted by concentrated hydrochloric acid at the ordinary temperature into the corresponding coumarins in a few hours, whilst, under the same conditions, *o*-coumaric acid and 4-methyl-*o*-coumaric acid remain practically unchanged even during several days. The tendency of β-alkyl-*o*-coumaric acids to change into coumarins is shown by the fact that the latter compounds slowly separate from solutions of the acids in aqueous sodium carbonate.

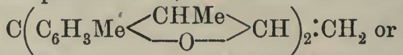
Ethyl o-*coumarate*, $C_{11}H_{12}O_3$, crystallises in small, compact plates, m. p. 87°; the *sodium* salt crystallises in yellow leaflets. *Ethyl* 4-*methyl*-o-*coumarate*, $C_{12}H_{14}O_3$, crystallises in plates, m. p. 105°.

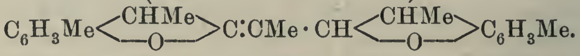
4-*Tolyloxy*-4 : 7-*dimethylhydrocoumarin*,



$$C_6H_3Me{<}\begin{matrix}CMe(OC_6H_4Me)\\ O\cdot CO\end{matrix}{>}CH_2,$$

is formed together with 4 : 7-dimethylcoumarin if in the preparation of the latter from *m*-cresol and ethyl acetoacetate the quantity of the sulphuric acid employed is less than that previously given (Abstr., 1906, i, 276). It crystallises in long, glistening prisms, m. p. 220°, and is converted by strong acids into *m*-cresol and 4 : 7-dimethylcoumarin.

3-[2 : 5-*Dimethylhydrocoumarilyl*]-4 : 7-*dimethylcoumarin*, $C_{22}H_{20}O_4$, crystallises in slender, white needles, m. p. 257° (decomp.). 1-[2 : 5-*Dimethylhydrocumarilyl*] - 2 : 5 - *dimethylhydrocoumarone*, $C_{21}H_{22}O_3$, crystallises in monoclinic prisms, m. p. 185·5°. The molten substance sets to a glassy mass, m. p. 93—95°; the liquefied substance again becomes solid at about 140°, and then has m. p. 185·5°. The *hydrobromide*, $C_{21}H_{22}O_3$,HBr, forms yellow crystals; the *oxime*, $C_{21}H_{23}O_3N$, crystallises in small plates, m. p. 220°; the *phenylhydrazone*, $C_{27}H_{28}O_2N_2$, forms slender, pale yellow needles, m. p. 198°. The ketone, $C_{21}H_{22}O_3$, when treated with magnesium methyl iodide and then with dilute sulphuric acid, is converted into a *substance*, having the formula  $C\left(C_6H_3Me{<}\begin{matrix}CHMe\\ O\end{matrix}{>}CH\right)_2{:}CH_2$ or



$$C_6H_3Me{<}\begin{matrix}CHMe\\ O\end{matrix}{>}C{:}CMe\cdot CH{<}\begin{matrix}CHMe\\ O\end{matrix}{>}C_6H_3Me.$$

It forms large crystals, m. p. 145°. The ketone, $C_{21}H_{22}O_3$, yields a *methoxy*-derivative, $C_{22}H_{24}O_3$, crystallising in long, flat plates, m. p. 165°, and an *ethoxy*-derivative, $C_{23}H_{26}O_3$, crystallising in prisms, m. p. 156°.

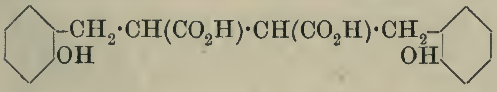
4 : 6-Dimethylcoumarin is converted by a hot aqueous solution of potassium hydroxide into β : 5-*dimethyl*-o-*coumaric acid*, $C_{11}H_{12}O_3$; it crystallises in small leaflets, decomposing with evolution of carbon dioxide at about 138°.

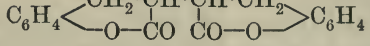
A *ketone*, $C_{21}H_{22}O_3$, is formed by the action of sodium ethoxide on 4 : 6-dimethylcoumarin. It is very similar in properties to the isomeric ketone derived from the 4 : 7-compound, forming compact, colourless crystals, m. p. 199°; the *oxime*, $C_{21}H_{23}O_3N$, crystallises in microscopic needles, m. p. 120°.

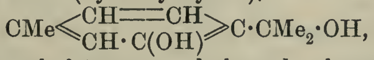
4 : 7-*Dimethyl*-3-*ethylcoumarin*, $C_{13}H_{14}O_2$, prepared by the action of concentrated sulphuric acid on a mixture of ethyl ethylacetoacetate and *m*-cresol, crystallises in long, spear-shaped needles, m. p. 87°.

3-*Benzyl*-4 : 7-*dimethylcoumarin*, $C_{18}H_{16}O_2$, prepared from ethyl benzylacetoacetate and *m*-cresol, crystallises in long, white needles, m. p. 117°. W. H. G.

Reduction of Coumarins with Zinc Dust in Alkaline Solution. KARL FRIES and G. FICKEWIRTH (*Annalen*, 1908, **362**, 30—48).—With the object of finding a simple method of preparing hydrocoumarins from coumarins, reduction by means of zinc dust in alkaline solution was tried, but without success. The results obtained show, however, that derivatives of coumarin containing an alkyl group in the pyrone ring are quite different in their chemical behaviour from coumarin itself.

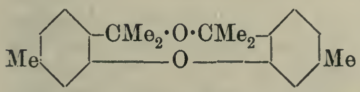


Coumarin is converted by zinc dust in alkaline solution chiefly into melilotic acid, but at the same time two isomeric tetrahydrodicoumaric acids are formed, namely, α- and β-tetrahydrodicoumaric acids, having the annexed formula. Each acid yields a tetrahydrodicoumarin, and these are consequently α- and β-tetrahydrocoumarins,  $C_6H_4\left<\begin{matrix}CH_2\cdot CH\cdot CH\cdot CH_2\\ -O-CO\quad CO-O-\end{matrix}\right>C_6H_4$ (compare Dyson, Trans., 1887, 51, 61). When 4 : 7-dimethylcoumarin is treated in the same way as coumarin, it yields 2-hydroxy-4-methylphenyldimethylcarbinol (hydroxythymol),



$$CMe\left<\begin{matrix}CH{=\!=}CH\\ CH\cdot C(OH)\end{matrix}\right>C\cdot CMe_2\cdot OH,$$

2-hydroxy-β : 4-dimethylstyrene, and thymol; the quantity of each substance formed depends on the duration of the action, the first compound formed being hydroxythymol. The part played by the zinc dust in the formation of the latter substance is not yet clear, for, although the formation of this alcohol is not due to simple reduction, yet the reaction proceeds in a different direction when the zinc dust is not present. It is probable that at first the 4 : 7-dimethylcoumarin is converted into β : 4-dimethyl-*o*-coumaric acid, which by the addition of water changes into β : 2-hydroxy-4-methylphenyl-β-methylhydracrylic acid, $OH\cdot C_6H_3Me\cdot CMe(OH)\cdot CH_2\cdot CO_2H$; the latter substance then loses carbon dioxide, yielding hydroxythymol. Since hydroxythymol, when heated, readily loses water, yielding 2-hydroxy-β : 4-dimethylstyrene or its polymeride (compare this vol., i, 160), it is evidently a tertiary alcohol having the formula given above. Although hydrochloric acid and hydrobromic acid convert hydroxythymol into the polymerised form of 2-hydroxy-α : 4-dimethylstyrene, hydriodic acid acts on it, forming a substance identical with the condensation product obtained by Gaebel (*Diss.*, Marburg, 1903) from *m*-cresol and acetone, to which the annexed formula was assigned. The normal reduction product of 4 : 7-dimethylcoumarin, namely, β : 4-dimethylhydrocoumaric acid, is obtained by using sodium amalgam as the reducing agent. This acid is very unstable, and readily changes into 4 : 7-dimethylhydrocoumarin.



4 : 6-Dimethylcoumarin is converted by zinc dust and alkali into 2-hydroxy-5-methylphenyldimethylcarbinol and 6-hydroxy-α : 3-dimethylstyrene (compare this vol., i, 160). The compound corresponding with thymol, namely, 2-hydroxy-5-methylcumene, seems to be formed only with difficulty, and has not yet been obtained pure.

3 : 4 : 7-Trimethylcoumarin remains practically unattacked by zinc dust in alkaline solution.

α-Tetrahydrodicoumaric acid, $C_{18}H_{18}O_6$, crystallises in plates, m. p.

280—282°. When heated alone for some time at 280°, or in acetic acid, it is converted into *a-tetrahydrodicoumarin*, $C_{18}H_{14}O_4$, crystallising in glistening needles, m. p. 284°.

β-Tetrahydrodicoumaric acid, $C_{18}H_{18}O_6$, forms compact prisms, m. p. 158°.

β-Tetrahydrodicoumarin, $C_{18}H_{14}O_4$, crystallises in glistening, slender needles, m. p. 256°.

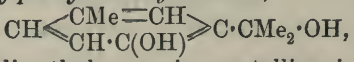
2-*Hydroxy*-4-*methylphenyldimethylcarbinol* (*hydroxythymol*),

$$C_{10}H_{14}O_2,$$

forms small, glistening, spear-shaped crystals, m. p. 64°. It is converted by hydriodic acid into a *substance*, $C_{20}H_{24}O_2$, crystallising in colourless, compact prisms, m. p. 132°. A *substance*, $(C_{10}H_{13}O)_n$, crystallising in small leaflets, m. p. 186°, is formed, together with hydroxythymol, by the action of zinc dust on 4 : 7-dimethylcoumarin in alkaline solution; mol.-wt. determinations by the boiling-point method point to *n* being 2.

β : 4-*Dimethyl*-o-*hydrocoumaric acid*, $C_{11}H_{14}O_3$, crystallises in hook-like needles, m. p. 98°; it loses water when heated, yielding 4 : 7-*dimethylhydrocoumarin*, obtained as an oil. If, during the reduction of 4 : 7-dimethylcoumarin with sodium amalgam, the liquid is kept slightly acid by means of acetic acid, a small quantity of a *substance*, m. p. 250°, is obtained. It is probably a tetramethyltetrahydrodicoumarin.

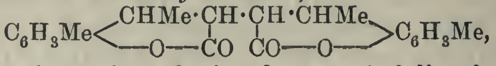
2-*Hydroxy*-5-*methylphenyldimethylcarbinol*,



$$CH{<}\genfrac{}{}{0pt}{}{CMe{=}CH}{CH\cdot C(OH)}{>}C\cdot CMe_2\cdot OH,$$

prepared from 4 : 6-dimethylcoumarin, crystallises in rosettes of small, glistening prisms, m. p. 82°.

a-Tetrahydrodi-4 : 6-*dimethylcoumarin*,



$$C_6H_3Me{<}\genfrac{}{}{0pt}{}{CHMe\cdot CH\cdot CH\cdot CHMe}{—O—CO\quad CO—O—}{>}C_6H_3Me,$$

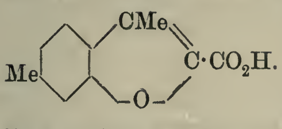
produced by the action of zinc dust on 4 : 6-dimethylcoumarin in alkaline solution, forms small needles, m. p. 284°. The *β-isomeride* is best prepared from *β* : 5-dimethylcoumaric acid; it forms small, colourless crystals, m. p. 254°. W. H. G.

Coumarone and Hydrocoumarone Derivatives from 4 : 7-Dimethylcoumarin.

KARL FRIES and G. FICKEWIRTH (*Annalen*, 1908, 362, 49—53).—The object of this investigation was the preparation of 2 : 5-dimethylhydrocoumarone, the latter being required for purposes of identification. This substance was first prepared by von Baeyer and Seuffert (Abstr., 1901, i, 216) by a method which gives but a poor yield. It was therefore obtained by reducing 2 : 5-dimethylcoumarilic acid to 2 : 5-dimethylhydrocoumarilic acid, which, when distilled with soda-lime, yields 2 : 5-dimethylhydrocoumarone.

4 : 7-Dimethylcoumarin is converted by bromine in chloroform into 3-*bromo*-4 : 7-*dimethylcoumarin*, $C_{11}H_9O_2Br$; it crystallises in long, white, silky needles, m. p. 138°, and is converted by a boiling alcoholic

solution of potassium hydroxide into 2 : 5-*dimethylcoumarilic acid.* The latter substance forms small, compact crystals or oblique-angled plates, m. p. about 212° (decomp.); the *ethyl* ester crystallises in small, slender needles, m. p. 38°. The acid, when distilled with soda-lime, yields 2 : 5-dimethylcoumarone, b. p. 218° (compare Stoemer, Abstr., 1900, i, 650).



2 : 5-*Dimethylhydrocoumarilic acid*, $C_{11}H_{12}O_3$, is obtained by reducing 2 : 5-dimethylcoumarilic acid with sodium amalgam. It forms small crystals, m. p. 95°, and, when distilled with soda-lime, yields 2 : 5-dimethylhydrocoumarone, $C_{10}H_{12}O$, an oil, b. p. 222°.

W. H. G.

Preparation of Double Salts from Caffeine and Alkali Metaphosphates. F. Hoffmann-La Roche & Cie (D.R.-P. 194533).—Caffeine and the alkali metals form soluble, stable dimetaphosphates.

Caffeine sodium dimetaphosphate, $C_8H_{10}O_2N_4,NaHP_2O_6$, is prepared by adding caffeine to an aqueous solution of sodium hydrogen dimetaphosphate and evaporating to dryness under reduced pressure.

G. T. M.

The Alkaloids of Chinese Corydalis Tubers. K. Makoshi (*Arch. Pharm.*, 1908, **246**, 381—400).—After much labour, corydaline, corybulbine, protopine, dehydrocorydaline (not hitherto known to occur naturally), and two new alkaloids were isolated. The first new *alkaloid*, $C_{20}H_{17}O_4N$, is an isomeride of berberine, and a quaternary base; the *hydrochloride*, $C_{20}H_{18}O_4NCl,2H_2O$, forms red needles, resembling sanguinarine hydrochloride, but is not precipitated by ammonia; *aurichloride*, $C_{20}H_{18}O_4NCl,AuCl_3$, reddish-brown needles, decomposing above 280° without melting. By zinc and hydrochloric acid, this alkaloid is reduced to a *substance*, $C_{20}H_{21}O_4N$, colourless needles, m. p. 218—219°, not identical with hydroberberine.

The second new *alkaloid*, greyish-white needles, m. p. 197—199°, was only obtained in minute quantity, and is not identical with bulbocapnine, since it gives different colour reactions. G. B.

Does Crystallisable Cocaine Occur in Java Coca? Anne W. K. de Jong (*Chem. Weekblad*, 1908, **5**, 666—668).—Samples of the alkaloid obtained from both the old and young leaves of Java coca contain cocaine, the percentage being higher in that derived from the former source. A. J. W.

Oxidation by means of Picric Acid. Indulines from Aniline. A. Bacovescu (*Chem. Zentr.*, 1908, i, 2034—2035; from *Buletinul d. Chimie*, 1908, **10**, 3—5).—When aniline is successively heated with picric acid to about 225° and the mass purified from chloroform and ether, two substances, probably indulines, are obtained.

The reaction also takes place in the presence of hydrogen chloride. One substance is greyish-black, the other brown, and both dissolve in concentrated sulphuric or acetic acid, giving a blue solution.

J. V. E.

Preparation of Halogenated Anilides. A. Mannino and L. di Donato (*Gazzetta*, 1908, 38, ii, 20—31).—The authors have applied the method used by Verda (Abstr., 1903, i, 21) to the preparation of halogenated derivatives of various acetanilides. The latter were treated with mixtures of nitric acid (D 1·398) and hydrochloric (D 1·19) or hydrobromic acid (D 1·48) in various proportions. As a rule, these acid mixtures effect only a chlorinating or brominating action, but in some cases, for example, aceto-*α*-naphthalide, a nitro-group is introduced into the molecule. It is remarkable that, in these reactions, hydrolysis of the acetyl group never occurs, although this takes place easily when the acetanilides are heated with hydrochloric acid alone. The products obtained are individual compounds in a pure state, and the yields are almost quantitative.

With acetanilide and nitric and hydrochloric acids, 2 : 4-dichloroacetanilide is obtained if the action is restricted, and 2 : 4 : 6-trichloroacetanilide if the action is prolonged. With nitric and hydrobromic acids, 2 : 4-dibromoacetanilide is formed. With *o*-chloroacetanilide, the product is 2 : 4 : 6-trichloroacetanilide or 2-chloro-4-bromoacetanilide. *m*-Chloroacetanilide yields (1) a *dichloroacetanilide*,

$$C_8H_7ONCl_2,$$

crystallising from alcohol in white needles, m. p. 187—188°, and probably not identical with 3 : 5-dichloroacetanilide, also melting at 187°, since under the above conditions the halogen generally enters in the *o*- or *p*-position to the NHAc group; (2) 3-*chloro*-2-*bromoacetanilide* (?), $C_8H_7ONClBr$, which crystallises from 60% acetic acid in needles, m. p. 105—107°. *p*-Chloroacetanilide yields 2 : 4 : 6-trichloroacetanilide or 4-chloro-2-bromoacetanilide. *m*-Bromoacetanilide gives 4 : 6-*dichloro*-3-*bromoacetanilide* (?), $C_8H_6ONCl_2Br$, which crystallises from alcohol in tufts of flesh-coloured needles, m. p. 194—195°, or 2 : 4 : 5-tribromoacetanilide. With *m*-nitroacetanilide a chlorodinitroacetanilide (?), m. p. about 200°, is formed. *p*-Nitroacetanilide yields 2-chloro-4-nitroacetanilide or a yellow bromo-derivative, m. p. about 115°, which was not obtained sufficiently pure to analyse.

Aceto-*o*-toluidide yields a dichloroaceto-*o*-toluidide, m. p. 155—156° (compare Verda, *loc. cit.*), or 5-bromo-2-acetotoluidide. Aceto-*p*-toluidide gives (1) 2 : 3 : 6- or 2 : 3 : 5-*trichloroaceto*-p-*toluidide*, $C_9H_8ONCl_3$, which separates from alcohol in crystals, m. p. 178—180°, and (2) 2 : 6-*dibromoaceto*-p-*toluidide*, $C_9H_8ONBr_2$.

Aceto-*m*-xylidide gives (1) 3 : 5 : 6-*trichloroaceto*-m-*xylidide*,

$$C_{10}H_{10}ONCl_3,$$

which crystallises from aqueous alcohol in white needles, m. p. 190—192°, and, when boiled with dilute hydrochloric acid, yields the corresponding *trichloro*-m-*xylidine*, m. p. 203°, or (2) 3 : 5 : 6-*tribromoaceto*-m-*xylidide*, $C_{10}H_{10}ONBr_3$, which separates from alcohol in crystals, m. p. 246—248°.

Aceto-α-naphthalide yields (1) the chloronitroaceto-α-naphthalide, m. p. 219°, which was prepared by Verda (*loc. cit.*), which, on boiling with dilute hydrochloric acid in alcoholic solution, gives a *compound*, $C_{10}H_7O_2N_2Cl$, crystallising from alcohol in yellow needles, m. p. about 230°, or (2) 3 : 8-dibromoaceto-α-naphthalide. Aceto-β-naphthalide gives (1) a red, oily chloro-derivative; (2) a tribromoaceto-β-naphthalide, m. p. 250° (decomp.), which gives, on hydrolysis, a compound, m. p. 125°; since 1 : 3 : 6-tribromo-β-naphthylamine has m. p. 143°, it is probable that the tribromoaceto-β-naphthalide is not the 1 : 3 : 6-compound which has been described as having the m. p. 250°.

T. H. P.

Resolution of Racemic Amines by means of Camphoramic Acids. Mlle. G. Freylon (*Ann. Chim. Phys.*, 1908, [viii], 15, 140—144).—According to Wallach (Abstr., 1906, i, 160), primary amines can be prepared by the addition of formic or acetic acid to a mixture of ammonium formate with an aldehyde or ketone. The author finds, however, that this method does not serve for the preparation of α-phenylethylamine, which can be obtained in a yield equal to 50% of the ketone employed by heating 10 grams of acetophenone with 20 grams of pure, dry ammonium formate to 180—190° for six hours.

When condensed with camphoric anhydride, α-phenylethylamine yields a mixture of the two stereoisomeric camphoramic acids, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot CHMePh$, which, by fractional crystallisation, can be separated into: (1) a dextro-fraction, $C_{18}H_{25}O_3N$, $[\alpha]_D^{20}$ + 64·92°, and (2) a lævo-fraction, $[\alpha]_D^{20}$ − 50·52°, both of which have m. p. 161—162°. When boiled with 30% hydrochloric acid, the *d*-compound yields the amine, b. p. 81°/15 mm., which gives a dextrorotatory hydrochloride, m. p. 159—160°, but was obtained in quantity too small to admit of analysis.

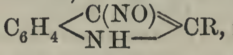
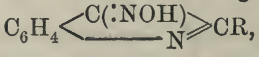
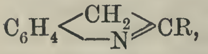
Thus, although the α-camphoramic acids are easily and rapidly prepared, they do not afford a good means for resolving racemic bases into their optically active components. With bases containing only aliphatic radicles, the resolution is more difficult than with aromatic compounds, so much so that in no case has more than one derivative exhibiting a constant m. p. and rotatory power been obtained (compare Locquin, Abstr., 1907, i, 593).

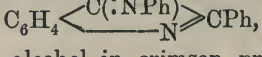
T. H. P.

New Method of Preparing some Simple Ethers. II. Th. van Hove (*Bull. Acad. roy. Belg.*, 1908, 540—551. Compare Abstr., 1907, i, 173).—The author has extended his investigation on the preparation of ethers by the action of quinoline hydrochloride on primary alcohols to secondary and tertiary alcohols, with the results that, whereas the secondary alcohol yields the corresponding ether and ethylene hydrocarbon, the tertiary alcohol yields ethylene hydrocarbons only. When *iso*propyl alcohol (1 mol.) is heated with quinoline hydrochloride (0·2 mol.) in sealed tubes at 160° for eight days, the products consist of *iso*propyl ether, *iso*propyl chloride, and propylene, together with an iso*propylquinoline* and *diiso*propylquinoline*. The *iso*propyl ether, b. p. 68—68·2°, $D^{16\cdot 2}$ 0·7349 (Zander, Abstr., 1882, 1259, gives $D^{20\cdot8}$ 0·7247), obtained amounted to 24·5% of the theoretical yield; the iso*propylquinoline*, b. p. 280—300°, yielded a *picrate*, m. p. 160—161°, and is therefore not identical with any of the *iso*propylquinolines already described (Widman, Abstr., 1886, 465; Döbner, Abstr., 1887, 504; Spady, Abstr., 1886, 263); *di*iso*propylquinoline*, b. p. 300—320°, forms a *picrate*, m. p. 226—228°.

When trimethylcarbinol is heated for three days at 160° with quinoline hydrochloride, the principal products consist of *iso*butylene and di*iso*butylene. M. A. W.

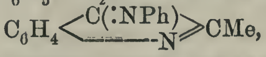
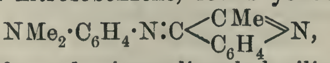
Catalytic Action of Finely-divided Metals on Compounds containing Nitrogen. Maurice Padoa and G. Scagliarini (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 728—731).—Whereas 2-methylindole is obtained on passing quinoline vapour over reduced nickel heated at 260—280° (Abstr., 1906, i, 765), 3-methylindole is formed together with a little quinoline when tetrahydroquinoline is similarly treated. The action probably occurs owing to the intermediate formation of propylaniline by the breaking of bond 4—5, or of 2-methylamino-1-ethylbenzene by the breaking of bond 2—3, probably the latter, because propylaniline does not produce a methylindole when heated with nickel at 300°. W. A. D.

Indoles. Angelo Angeli and Eugenio Morelli (*Atti R. Accad. Lincei*, 1908, [v], 17, i, 697—702).—The view that 3-nitrosoindoles are true nitroso-derivatives,  $C_6H_4\left<\begin{array}{c}C(NO)\\NH\end{array}\right>CR$, is improbable in view of the fact that either the silver or sodium salt gives with ethyl iodide only one ethyl derivative; that obtained from 3-nitroso-2-phenylindole is red, and has m. p. 45°. The structure of the nitrosoindoles is discussed at some length; they are probably best regarded as oximes,  $C_6H_4\left<\begin{array}{c}C(:NOH)\\N\end{array}\right>CR$, derived from the tautomeric form,  $C_6H_4\left<\begin{array}{c}CH_2\\N\end{array}\right>CR$, of the indoles. This view is confirmed by the fact that 2-phenylindole reacts with nitrosobenzene in alcoholic solution in presence of traces of alkali, forming the *compound*,



$$C_6H_4\left<\begin{array}{c}C(:NPh)\\N\end{array}\right>CPh,$$

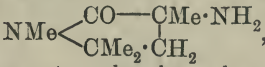
which crystallises from alcohol in crimson prisms, m. p. 155°. The action is compared with that of phenylacetonitrile and nitrosobenzene, $CH_2Ph{\cdot}CN + NO{\cdot}C_6H_5 = H_2O + NPh{:}CPh{\cdot}CN$.

The *compound*,  $C_6H_4\left<\begin{array}{c}C(:NPh)\\N\end{array}\right>CMe$, prepared from 2-methylindole and nitrosobenzene, forms yellow crystals, m. p. 183°. The *compound*,  $NMe_2{\cdot}C_6H_4{\cdot}N{:}C\left<\begin{array}{c}CMe\\C_6H_4\end{array}\right>N$, obtained similarly from 2-methylindole and nitrosodimethylaniline, forms red needles, m. p. 185°. W. A. D.

Preparation of Anthranil. Kalle & Co. (D.R.-P. 194364. Compare Abstr., 1907, i, 908).—The dimercury derivative of *o*-nitrotoluene forms a yellow chloride when mixed with 10% hydrochloric acid, and this product ,when added to stronger hydrochloric acid (D 1·185), furnishes the hydrochloride of anthranil, from which this amide can be purified by distillation in steam. G. T. M.

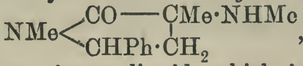
Aminopyrrolidone Derivatives from Mesityl Oxide and from Benzylideneacetone. MORITZ KOHN (*Monatsh.*, 1908, 29, 497—508).—Bucherer's and Zelinsky's modifications of Strecker's original method for the production of α-amino-acids have been applied by the author to β-amino-ketones, with the result that aminopyrrolidone derivatives are obtained instead of the expected α : γ-diamino-acids.

The interaction of aqueous methyldiacetonamine, powdered potassium cyanide (1 mol.), and concentrated aqueous ammonium chloride (1 mol.) at 5—10° leads, after hydrolysis of the diaminonitrile by concentrated hydrochloric acid, to the formation of 4-*amino*-5-*keto*-1 : 2 : 2 : 4-*tetramethylpyrrolidine*,



$\mathrm{NMe}<\begin{matrix}\mathrm{CO}—\mathrm{CMe\cdot NH_2}\\ \mathrm{CMe_2\cdot CH_2}\end{matrix}$, b. p. 140—143°/17 mm., which is soluble in water, absorbs carbon dioxide, and forms a *phenylthiocarbamide*, m. p. 180—181°. By using methylamine hydrochloride in the place of ammonium chloride in the preceding reaction, 4-*methylamino*-5-*keto*-1 : 2 : 2 : 4-*tetramethylpyrrolidine*, $C_9H_{18}ON_2$, b. p. 128—130°/15—16 mm., is obtained, which also absorbs water or carbon dioxide, and yields a *phenylthiocarbamide*, m. p. 132—135°, and an *acetyl* derivative, m. p. 123—125·5°. 4-*Dimethylamino*-5-*keto*-1 : 2 : 2 : 4-*tetramethylpyrrolidine*, b. p. 130—140°/13 mm., obtained in a similar manner by using an aqueous-alcoholic solution of dimethylamine hydrochloride, forms a *platinichloride* and a *methiodide*, from which the corresponding *aurichloride* and *platinichloride* are obtained.

The constitution of the additive compound of benzylideneacetone and methylamine has been shown to be $CH_3\cdot CO\cdot CH_2\cdot CHPh\cdot NHMe$, since it can be converted by potassium cyanide and methylamine hydrochloride and subsequent hydrolysis into 4-*methylamino*-5-*keto*-2-*phenyl*-1 : 4-*dimethylpyrrolidine*,



$\mathrm{NMe}<\begin{matrix}\mathrm{CO}—\mathrm{CMe\cdot NHMe}\\ \mathrm{CHPh\cdot CH_2}\end{matrix}$, b. p. 181°/13 mm., a colourless, odourless, viscous liquid, which is soluble in water, absorbs carbon dioxide, and forms a crystalline *phenylthiocarbamide.* C. S.

Stereoisomeric Chloroimino-acid Esters. WILLIS STOSE HILPERT (*Amer. Chem. J.*, 1908, 40, 150—194).—Stieglitz and Earle (Abstr., 1904, i, 39) have shown that methyl chloroimino-*m*-nitrobenzoate exists in two stereoisomeric modifications, and Stieglitz and Hale have recently found (unpublished) that the corresponding ethyl ester exhibits the same phenomenon. The author now finds that methyl and ethyl chloroimino-*p*-nitrobenzoates, methyl chloroimino-2-nitro-*p*-toluate, and methyl and ethyl chloroimino-β-naphthoates also exist in stereoisomeric modifications, but no stereoisomerides are obtainable in the case of methyl chloroimino-*p*-bromo-*m*-nitrobenzoate and methyl chloroimino-*p*-bromobenzoate. In the case of the first three pairs of stereoisomerides, the less stable form can be transformed into the more stable one by the action of chlorine, and the converse process also is possible to a small extent. In the case of the naphthalene derivatives, the change is brought about by boiling water. Further details are given for the separation of α- and β-methyl chloroimino-*m*-nitrobenzoates and for the transformation of one form into the other.

When *p*-nitrobenzonitrile is treated with methyl alcohol in benzene solution, it yields *methyl imino*-p-*nitrobenzoate*, a white, crystalline substance, m. p. 93—94°, which, with hypochlorous acid, gives *methyl chloroimino*-p-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot C(OMe)\colon NCl$.

The crude substance is fractionally precipitated from its chloroform solution by light petroleum, whereby the α-(*syn.*-)form is precipitated in needles, m. p. 99—100°, and the mother liquor yields the more stable β-(*anti*-)form in plates, m. p. 76°. *Ethyl chloroimino*-p-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot C(OEt)\colon NCl$, is prepared similarly by the action of hypochlorous acid on the imino-ester obtained from *p*-nitrobenzonitrile and ethyl alcohol. By the same process of fractionation as used for the methyl ester, the α-(*syn.*-)form was almost exclusively obtained in needles, m. p. 98—99°. The β-(*anti*-)form, which crystallised only to a very small extent along with the α-form, was isolated mechanically; it occurs in plates, m. p. 90°, and is the more unstable modification, being readily transformed into the α-form by chlorine. n-*Propyl chloroimino*-p-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot C(OPr^{\alpha})\colon NCl$, is an oil. *Methyl imino-2-nitro*-p-*toluate*, prepared from 2-nitro-*p*-tolunitrile and methyl alcohol, is a white, crystalline solid, m. p. 60—61°; the *hydrochloride* was analysed. On treatment with hypochlorous acid, the free ester yields *methyl chloroimino-2-nitro*-p-*toluate*,

$$NO_2\cdot C_6H_3Me\cdot C(OMe)\colon NCl,$$

which, when fractionally precipitated by light petroleum from its chloroform solution, yielded a mixture of the α-(*syn.*-)form in plates, m. p. 84—85°, and the β-(*anti*-)form in needles, m. p. 71°. The α-modification is readily transformed by chlorine into the more stable β-form.

Methyl chloroimino-p-*toluate*, $C_6H_4Me\cdot C(OMe)\colon NCl$, is a colourless oil.

Methyl chloroimino-β-naphthoate, $C_{10}H_7\cdot C(OMe)\colon NCl$, prepared by chlorinating methyl imino-β-naphthoate, is separated into the two modifications by adding light petroleum to its chloroform solution. The α-form is precipitated in minute crystals, m. p. 125°, and from the filtrate is obtained the β-form in large, thin plates, m. p. 72°. By heating with water, each modification is partly transformed into the other, probably by the action of a trace of hypochlorous acid or chlorine liberated from the chloroimino-ester.

Ethyl chloroimino-β-naphthoate (Slosson, Abstr., 1903, i, 475), when prepared by the hypochlorous acid method, yields an α-(*syn.*-)variety, m. p. 72°, and a substance crystallising in needles, m. p. 39°, which is probably a mixture of both forms.

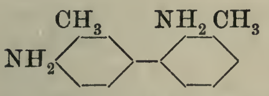
Methyl chloroimino-p-*bromobenzoate*, $C_6H_4Br\cdot C(OMe)\colon NCl$, crystallises in plates and needles, m. p. 60°; it does not, however, occur in two stereoisomeric modifications. *Methyl chloroimino*-p-*bromo*-m-*nitrobenzoate*, $NO_2\cdot C_6H_3Br\cdot C(OMe)\colon NCl$, also crystallises in plates and needles, m. p. 95°, which are not stereoisomeric. *Methyl chloroimino*-p-*anisate*, $MeO\cdot C_6H_4\cdot C(OMe)\colon NCl$, prepared from *methyl iminoanisate hydrochloride*, is a pale yellow oil with a sharp odour.

Methyl bromoimino-m-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot C(OMe)\colon NBr$, prepared from methyl imino-*m*-nitrobenzoate and hypobromous acid, crystallises in plates, m. p. 99·5°, and needles, m. p. 101°, which are not stereoisomeric. *Methyl bromoimino-β-naphthoate*,

$$C_{10}H_7\cdot C(OMe)\colon NBr,$$

has m. p. 99—100°. J. C. C.

The Transformation of Hydrazotoluene into Tolidine. J. P. van Loon (*Chem. Weekblad*, 1908, 5, 689—698).—The transformation of hydrazotoluene into tolidine has been investigated quantitatively, and it has been found that 100 grams of hydrazotoluene yield 87·4 grams of tolidine, 2 grams of azotoluene, and 2 grams of toluidine. A small proportion of an isomeride of tolidine, probably of the annexed formula, is also formed, but has not been obtained free from tolidine. The estimation of the tolidine was effected by precipitation as sulphate from hydrochloric acid solution by magnesium sulphate, a correction being necessary on account of tolidine sulphate being appreciably soluble in cold water. The value of the correction factor was ascertained by experiments on the solubility of the sulphate at certain temperatures. A. J. W.



Replacement of Hydroxyl Groups by Hydrazino-groups. Hartwig Franzen and Th. Eichler (*J. pr. Chem.*, 1908, [ii], 78, 157—164. Compare Abstr., 1905, i, 244, and following abstract).—It has not been found possible to replace the hydroxyl groups in catechol and quinol by hydrazino-residues, or yet to transform 1 : 3 : 4-tolylenediamine into the corresponding hydrazine derivative.

Dibenzylidene-1 : 3-*phenylenedihydrazine*, $C_6H_4(NH\cdot N\colon CHPh)_2$, obtained by the action of benzaldehyde on the crude product obtained by heating resorcinol, hydrazine sulphate, and a 50% solution of hydrazine hydrate for six hours to 110—120° in an atmosphere of hydrogen, crystallises from xylene and has m. p. 247—248°.

Pyruvic acid reacts with the same condensation product, yielding *dipyruvic acid*-m-*phenylenedihydrazine*, $C_6H_4(NH\cdot N\colon CMe\cdot CO_2H)_2$, in the form of a yellow solid, m. p. 191°.

Hydrazine salicylate, $OH\cdot C_6H_4\cdot CO_2H,N_2H_4$, forms colourless crystals, m. p. 106°, which, when heated by means of nitrobenzene vapour, yield 3-keto-1 : 3-dihydroindazole (Fischer, Abstr., 1882, 1068). Salicylhydrazide when heated in the same manner yields the indazole in addition to *disalicylhydrazide*, $N_2H_2(CO\cdot C_6H_4\cdot OH)_2$, m. p. 301°.

Hydrazine-o-hydroxytoluate, $OH\cdot C_6H_3Me\cdot CO_2H,N_2H_4$ [$Me\colon OH\colon CO_2H = 1:2:3$], has m. p. 133—134°; the isomeric *meta*-compound [1 : 3 : 4] 137—138°, and the *para*-compound [1 : 4 : 3], 130°. When these salts are heated, they yield mixtures of hydrazino- and dihydroindazole derivatives, which so far have not been separated.

β-Hydroxynaphthoic acid hydrazide, $OH\cdot C_{10}H_6\cdot CO\cdot NH\cdot NH_2$ [2 : 3], crystallises from alcohol in yellow plates, m. p. 203—204° (decomp.), and yields a *benzylidene* derivative, $OH\cdot C_{10}H_6\cdot CO\cdot NH\cdot N{:}CHPh$, m. p. 224·5°. J. J. S.

7-Hydroxy-β-naphthylhydrazine. Hartwig Franzen and W. Deibel (*J. pr. Chem.*, 1908, [ii], 78, 143—157).—Although 2:3-dihydroxynaphthalene yields 2:3-naphthylenedihydrazine when heated with hydrazine hydrate, the isomeric 2 : 7-dihydroxy-derivative, under similar conditions, yields 7-hydroxy-β-naphthylhydrazine,

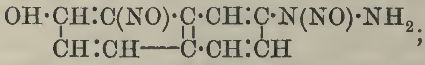
$$OH\cdot C_{10}H_6\cdot NH\cdot NH_2\,;$$

even when the latter compound is heated with hydrazine hydrate, a good yield of the dihydrazine derivative is not obtained.

This anomalous behaviour of the 2 : 7-dihydroxynaphthalene cannot be explained by supposing that one of the hydroxyl groups reacts as the tautomeric ketone, since ketones also condense readily with hydrazine.

The best yield of *7-hydroxy-β-naphthylhydrazine* is obtained when the dihydroxy-derivative, hydrazine sulphate, and a 45% solution of hydrazine hydrate are heated at 120—125° for eight hours in an atmosphere of hydrogen. It crystallises from water or alcohol in colourless plates, m. p. 176° (decomp.), and, when exposed to the air, turns red. It dissolves in acids, but not in alkalis or ether. The *hydrochloride*, $C_{10}H_{10}ON_2,HCl$, is readily soluble in water, and has m. p. 192°; the *sulphate* is somewhat less soluble, and has m. p. 232° (decomp.); the *nitrate* has m. p. 173° (decomp.), and also decomposes when kept for some time. When the finely-divided base, obtained by the addition of a little potassium hydroxide solution to its aqueous solution, is oxidised by aspirating air through the suspension, a dark red solution is formed, and this yields a red precipitate with carbon dioxide.

Nitrous acid transforms the base into a *dinitroso*-derivative, probably



$$\begin{array}{l} OH\cdot \underset{|}{C}H{:}C(NO)\cdot \underset{||}{C}\cdot CH{:}\underset{|}{C}\cdot N(NO)\cdot NH_2 \\ \quad CH{:}CH{-}{-}C\cdot CH{:}CH \end{array}$$

; it has m. p. 124°.

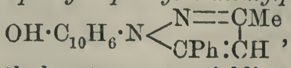
Benzaldehyde 7-hydroxy-β-naphthylhydrazone,

$$OH\cdot C_{10}H_6\cdot NH\cdot N{:}CHPh,$$

crystallises from benzene in pale yellow plates, m. p. 233°. The corresponding *o-hydroxybenzaldehyde* derivative, $C_{17}H_{14}O_2N_2$, has m. p. 223°.

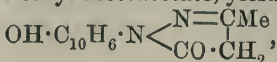
7-Hydroxy-β-naphthylsemicarbazide, $OH\cdot C_{10}H_6\cdot NH\cdot NH\cdot CO\cdot NH_2$, obtained by the action of a concentrated aqueous solution of potassium cyanate on the hydrazine derivative, crystallises from alcohol in reddish-violet needles, m. p. 228°. *7-Hydroxy-β-naphthylphenylthiosemicarbazide*, $OH\cdot C_{10}H_6\cdot NH\cdot NH\cdot CS\cdot NHPh$, obtained by the action of phenylthiocarbimide on the hydrazine, has m. p. 183°.

The base condenses with an alcoholic solution of benzoylacetone, yielding *7′-hydroxy-β-naphthyl-5-phenyl-3-methylpyrazole*,



$$OH\cdot C_{10}H_6\cdot N\Big\langle\begin{array}{l} N{=}{=}CMe \\ CPh{:}CH \end{array},$$

m. p. 199°, and with ethyl acetoacetate, yielding *7′-hydroxy-β-naphthyl-3-methylpyrazolone*,



$$OH\cdot C_{10}H_6\cdot N\Big\langle\begin{array}{l} N{=}CMe \\ CO\cdot CH_2 \end{array},$$

m. p. 243°.

7-*Chloro-β-naphthol*, $C_{10}H_6Cl{\cdot}OH$, can be prepared by dropping a hot solution of the hydroxyhydrazine into a boiling solution of copper sulphate; it crystallises from light petroleum in colourless plates, m. p. 126·5°. The corresponding *acetyl* derivative, $C_{10}H_6Cl{\cdot}OAc$, crystallises from toluene in colourless plates, m. p. 104·5°.

An acetic acid solution of the hydroxyhydrazine is oxidised by copper sulphate solution to β-naphthol.

7-*Amino-β-naphthol*, $OH{\cdot}C_{10}H_6{\cdot}NH_2$, obtained together with 2 : 7-naphthylenediamine by heating 2 : 7-dihydroxynaphthalene with ammonium sulphite and hydroxide in a reflux apparatus, has m. p. 201°.

In the preparation of 7-hydroxy-β-naphthylhydrazine, a small amount of 2 : 7-naphthylenedihydrazine is formed. This yields a *dibenzylidene* derivative, $C_{10}H_6(NH{\cdot}N{:}CHPh)_2$, m. p. 186·5°.

7-*Amino-β-naphthylhydrazine*, $NH_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}NH_2$, obtained by the action of hydrazine hydrate and sulphate on 2 : 7-naphthylenediamine, has m. p. 184°, and yields a *dibenzylidene* derivative,

$$CHPh{:}N{\cdot}C_{10}H_6{\cdot}NH{\cdot}N{:}CHPh,$$

m. p. 201·5°, and a *di-o-hydroxybenzylidene* derivative,

$$OH{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_{10}H_6{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH,$$

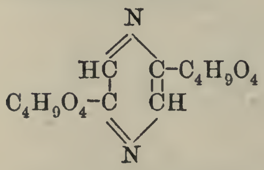
which begins to decompose at 169°. J. J. S.

Action of Nitrogen Peroxide on Aldehyde Phenylhydrazones. Roberto Ciusa and Ugo Pestalozza (*Atti R. Accad. Lincei*, 1908, [v], **17**, i, 840—846).—The action of nitrogen peroxide on aldehyde phenylhydrazones in ethereal solution yields the corresponding arylnitroformaldehyde phenylhydrazones in almost quantitative proportions: $CHAr{:}N_2HPh \longrightarrow NO_2{\cdot}CAr{:}N_2HPh$, small amounts of free aldehyde, diazobenzene nitrate, and oxidation products being also formed. The reaction affords a very convenient method of preparing arylnitroformaldehyde phenylhydrazones, being easier to carry out, and giving better yields of purer material, than the action of diazobenzene salts on the primary nitrohydrocarbons, or the action of nitrous acid on the phenylhydrazones. As regards the mechanism of the reaction, the nitro-group replaces the methinic hydrogen atom, a further proof being thus afforded of the peculiar activity of this hydrogen atom.

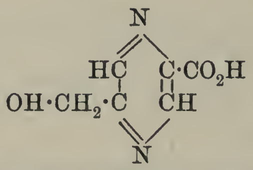
The phenylhydrazones on which the reaction was tried were those of benzaldehyde, *m*-nitrobenzaldehyde, anisaldehyde, and piperonal. The compound obtained in the last case was *nitromethylenedioxy-ω-benzaldehydephenylhydrazone*, $CH_2O_2{:}C_6H_3{\cdot}C(NO_2){:}N_2HPh$, which crystallises from a mixture of benzene and alcohol in ruby-red, prismatic needles, m. p. 119°, and dissolves in concentrated sulphuric acid, giving a violet coloration changing to red, and with alkalis, forming dark red solutions, from which it is re-precipitated by the addition of acid; the *potassium* salt is obtained as a golden-yellow, crystalline powder. T. H. P.

The Degradation of Lævulosazine (Ditetrahydroxybutylpyrazine) in the Animal Body. Karl Stolte (*Biochem. Zeitsch.*, 1908, **12**, 499—509).—After ingestion of lævulosazine, a product is excreted in the urine which gives with ferrous sulphate in acetic acid solution a carmine-red colour. The substance causing this reaction was isolated from rabbits' urine by concentrating it to a syrup and precipitating the inorganic salts with alcohol. On addition of a concentrated aqueous solution of copper acetate acidified with acetic acid, a copper salt was precipitated. This was dissolved in sodium hydroxide solution and decomposed by hydrogen sulphide, the filtrate from the sulphide decolorised by charcoal, and copper acetate in aqueous solution added. A crystalline precipitate was thereby obtained, which was identified as the copper salt of 2-hydroxymethylpyrazine-5-carboxylic acid. On oxidation with hydrogen peroxide in alkaline solution, it yielded pyrazine-2 : 5-dicarboxylic acid, m. p. 272—273°.

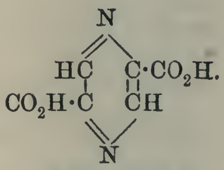
The relation of lævulosazine to these degradation products can be expressed as follows:



Lævulosazine.



2-Hydroxymethylpyrazine-5-carboxylic acid.



Pyrazine-2 : 5-dicarboxylic acid.

The constitution of the excreted product was also confirmed by the preparation of an acetyl derivative. The substance which sometimes in normal urine gives a red coloration with ferrous sulphate is not a pyrazine derivative. S. B. S.

Preparation of Certain Azines. GIACOMO PONZIO and R. GIOVETTI (*Gazzetta*, 1908, **38**, ii, 123—126; *Atti R. Accad. Sci. Torino*, 1908, **43**, 817—820).—The conclusion drawn by von Rothenburg (Abstr., 1893, i, 701), that when hydrazine acts on compounds containing the group $\colon NOH$ the latter is always replaced by $\colon N\cdot NH_2$, is inaccurate. Thus, from *iso*nitrosoacetone and hydrazine, the authors have obtained the corresponding azine,

$$NOH\colon CH\cdot CMe\colon N\cdot N\colon CMe\cdot CH\colon NOH,$$

and from the latter, by means of a simple and general reaction, the azines of mixed *iso*nitroso-ketones, $Me\cdot CO\cdot CAr\colon NOH$, which cannot be prepared directly. The latter compounds crystallise well, and are converted into mixed diketones, $CH_3\cdot CO\cdot CO\cdot Ar$, by the action of dilute acids, but are not transformable into pyrazolines.

iso*Nitrosoacetonazine*, $C_6H_{10}O_2N_4$, prepared by the action of powdered hydrazine sulphate (1 mol.) on a solution of *iso*nitrosoacetone (2 mols.) in 20% sodium hydroxide solution, separates from alcohol or water in crystals, m. p. 221° (decomp.).

iso*Nitrosophenylacetonazine*, $(NOH\colon CPh\cdot CMe\colon)_2N_2$, obtained by the interaction of *iso*nitrosoacetonazine and diazobenzene chloride (2 mols.) in 10% sodium hydroxide solution, crystallises from alcohol in yellowish-red needles, m. p. 187—188°, and yields hydrazine sulphate and phenyl methyl diketone when heated with 10% sulphuric acid.

iso*Nitroso*-p-*tolylacetonazine*, $[\mathrm{C_6H_4Me{\cdot}C(NOH){\cdot}CMe{:}}]_2\mathrm{N_2}$, prepared by treating *iso*nitrosoacetonazine in alkaline solution with diazo-*p*-toluene chloride, crystallises from alcohol in yellow laminæ, m. p. 198—199° (decomp.).

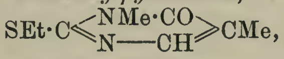
iso*Nitrosoanisylacetonazine*, $[\mathrm{OMe{\cdot}C_6H_4{\cdot}C(NOH){\cdot}CMe}]_2\mathrm{N_2}$, prepared in a similar manner to the preceding compounds, crystallises from alcohol in yellow prisms, m. p. 193—194° (decomp.), and yields hydrazine sulphate and *p*-anisyl methyl diketone, m. p. 44—45°, when distilled with 10% sulphuric acid. T. H. P.

Pyrimidines. XXXIII. Synthesis of *N*-Alkyl Derivatives of Cytosine, Thymine, and Uracil. Treat B. Johnson and Samuel H. Clapp (*J. Biol. Chem.*, 1908, 5, 49—70. Compare this vol., i, 692, 693).—Various *N*-alkyl derivatives of cytosine, thymine, and uracil have been synthesised on account of the occurrence of certain methylpurines in nature, and also on account of the relationship between methyluracils and the purines, theobromine and caffeine.

The introduction of methyl groups into these pyrimidine derivatives has a similar influence on their physical properties to that on the purines. They increase the solubility and lower the melting points. The 3-methyl pyrimidines melt at higher temperatures than the isomeric 1-methyl derivatives.

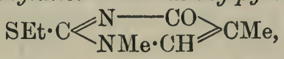
When 6-oxy-2-ethylthiol-5-methylpyrimidine is methylated by means of methyl iodide and alcoholic potassium hydroxide, a mixture of the two isomeric 1 : 5- and 3 : 5-dimethyl derivatives is obtained.

6-*Oxy*-2-*ethylthiol*-1 : 5-*dimethylpyrimidine*,



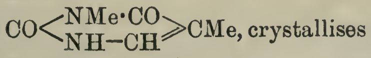
$$\mathrm{SEt{\cdot}C}\left\langle\begin{matrix}\mathrm{NMe{\cdot}CO}\\ \mathrm{N{-\!-}CH}\end{matrix}\right\rangle\mathrm{CMe},$$

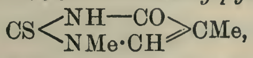
is less soluble, and crystallises from water in long, slender prisms, m. p. 65°. 6-*Oxy*-2-*ethylthiol*-3 : 5-*dimethylpyrimidine*,



$$\mathrm{SEt{\cdot}C}\left\langle\begin{matrix}\mathrm{N{-\!-}CO}\\ \mathrm{NMe{\cdot}CH}\end{matrix}\right\rangle\mathrm{CMe},$$

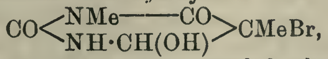
crystallises from benzene in colourless prisms, m. p. 156°. When hydrolysed with hydrobromic acid, each thio-derivative yields the corresponding thymine.

1-*Methylthymine*,  $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NMe{\cdot}CO}\\ \mathrm{NH{-}CH}\end{matrix}\right\rangle\mathrm{CMe}$, crystallises from water in stout prisms, m. p. 202—205° (decomp.), and the isomeric 3-*methylthymine* crystallises from the same solvent in prismatic needles or octahedral prisms, m. p. 280—282°. In the formation of the latter compound, a certain amount of 6-*oxy*-2-*thio*-3 : 5-*dimethylpyrimidine*,



$$\mathrm{CS}\left\langle\begin{matrix}\mathrm{NH{-}CO}\\ \mathrm{NMe{\cdot}CH}\end{matrix}\right\rangle\mathrm{CMe},$$

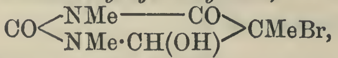
is also formed; it is less soluble in water than the methylthymine, and crystallises in needles, m. p. 229—230°.

Bromine water converts 1-methylthymine into 5-*bromo*-4-*hydroxy*-1-*methylhydrothymine*,  $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NMe{-\!-}CO}\\ \mathrm{NH{\cdot}CH(OH)}\end{matrix}\right\rangle\mathrm{CMeBr}$, which crystallises in stout prisms, m. p. 123—125°, when heated slowly. The corresponding 5-*nitro*-derivative, $\mathrm{C_6H_9O_5N_3}$, obtained by the action of nitric acid on the base, forms well-developed prisms, m. p. 135—136° (decomp.).

The isomeric 5-*nitro*-4-*hydroxy*-3-*methylhydrothymine*, obtained by the action of nitric acid on 3-methylthymine, crystallises in large prisms, which decompose at 178—181°.

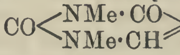
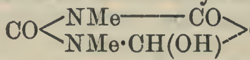
The *monopotassium* derivative of thymine, $C_5H_5O_2N_2K$, crystallises from alcohol in long needles.

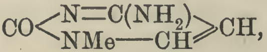
1 : 3-Dimethylthymine (Steudel, Abstr., 1901, i, 108) is most readily obtained by methylating thymine, and with bromine water yields 5-*bromo*-4-*hydroxy*-1 : 3-*dimethylhydrothymine*,

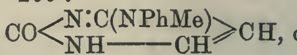
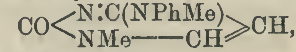


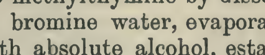
$$\mathrm{CO}<\begin{matrix}\mathrm{NMe}\text{——}\mathrm{CO}\\ \mathrm{NMe{\cdot}CH(OH)}\end{matrix}>\mathrm{CMeBr},$$

in the form of prisms, m. p. 132—133°.

Monopotassiumuracil, obtained by digesting uracil with the theoretical amount of alcoholic potassium hydroxide, has the composition $C_4H_3O_2N_2K,H_2O$, and loses its water of hydration at 120°. When uracil is methylated in the presence of potassium hydroxide, 1 : 3-*dimethyluracil*,  $\mathrm{CO}<\begin{matrix}\mathrm{NMe{\cdot}CO}\\ \mathrm{NMe{\cdot}CH}\end{matrix}>\mathrm{CH}$, which crystallises from a mixture of ether and alcohol in long, slender prisms, m. p. 121—122°, is obtained. With bromine water this base yields 5-*dibromo*-4-*hydroxy*-1 : 3-*dimethylhydrouracil*,  $\mathrm{CO}<\begin{matrix}\mathrm{NMe}\text{——}\mathrm{CO}\\ \mathrm{NMe{\cdot}CH(OH)}\end{matrix}>\mathrm{CBr_2}$, m. p. 135—136°, which is transformed into 5-*bromo*-1 : 3-*dimethyluracil* when digested with alcohol.

3-*Methylcytosine*,  $\mathrm{CO}<\begin{matrix}\mathrm{N{=}C(NH_2)}\\ \mathrm{NMe}\text{—}\mathrm{CH}\end{matrix}>\mathrm{CH}$, obtained by methylating cytosine, crystallises from methyl alcohol in prisms, decomp. 278—279°. The *platinichloride*, $(C_5H_7ON_3)_2H_2PtCl_6,2H_2O$, crystallises in slender prisms, and the *picrate* in long prisms, which decompose at 280° when heated slowly. 5-*Bromo*-3-*methyluracil*, $C_5H_5O_2N_2Br$, obtained by treating 3-methylcytosine with bromine and water and digesting the product with ethyl alcohol, crystallises from water in slender needles, which decompose at 255—260°.

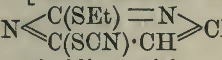
2-*Oxy*-6-*phenylmethylaminopyrimidine*,  $\mathrm{CO}<\begin{matrix}\mathrm{N{:}C(NPhMe)}\\ \mathrm{NH}\text{——}\mathrm{CH}\end{matrix}>\mathrm{CH}$, obtained by the action of methylaniline on 6-chloro-2-ethylthiolpyrimidine and digesting the product with hydrobromic acid, crystallises from alcohol in hexagonal plates, which do not decompose below 285°. When this base is methylated, it yields 2-*oxy*-6-*phenylmethylamino*-3-*methylpyrimidine*,  $\mathrm{CO}<\begin{matrix}\mathrm{N{:}C(NPhMe)}\\ \mathrm{NMe}\text{——}\mathrm{CH}\end{matrix}>\mathrm{CH}$, which crystallises in striated prisms, m. p. 186—187°.

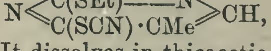
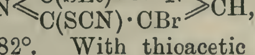
3 : 5-Dimethylcytosine,  $\mathrm{CO}<\begin{matrix}\mathrm{N{:}C(NH_2)}\\ \mathrm{NMe}\text{—}\mathrm{CH}\end{matrix}>\mathrm{CMe}$, obtained by methylating 5-methylcytosine (Abstr., 1904, i, 624), crystallises from methyl alcohol in prisms, which decompose at 300—310°.

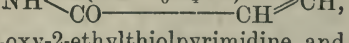
The formation of the 3-methylthymine by dissolving 3 : 5-dimethylcytosine in concentrated bromine water, evaporating to dryness, and digesting the product with absolute alcohol, establishes the positions of the methyl groups in 3 : 5-dimethylcytosine.

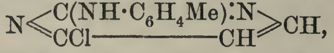
[With N. A. Martin.]—Electrical conductivity measurements have been made with thymine and its *N*-methyl derivatives. The conductivities tend to increase with the length of time the solutions are kept, especially in the case of 1- and 3-methylthymines. J. J. S.

Pyrimidines. XXXV. Action of Potassium Thiocyanate on Some Imide Chlorides. Treat B. Johnson and Walter F. Storey (*Amer. Chem. J.*, 1908, **40**, 131—147).—Wheeler and Bristol (Abstr., 1905, i, 483) have shown that 6-chloro-2-ethylthiolpyrimidine, 6-chloro-2-ethylthiol-5-methylpyrimidine, and 6-chloro-5-bromo-2-ethylthiolpyrimidine give thiocarbimido-derivatives when treated with potassium thiocyanate, but the intermediate formation of thiocyanates was not observed. Johnson and McCollum, however (Abstr., 1906, i, 768), found that 6-chloro-5-ethoxy-2-ethylthiolpyrimidine yields the 6-thiocyano-derivative, which can be transformed into the corresponding 6-thiocarbimido-derivative. The present authors have now examined the behaviour of potassium thiocyanate towards 6-chloro-2-*p*-toluidinopyrimidine, 6-chloro-2-*o*-toluidinopyrimidine, and 6-chloro-2-*p*-tolyl-4-methylpyrimidine; the two forms do not react with potassium thiocyanate, but the latter gives the corresponding thiocyano-derivative, which can be transformed into the isomeric thiocarbimido compound. Moreover, the substances examined by Wheeler and Bristol yield thiocyano-derivatives, readily transformed into the thiocarbimido-isomerides when the time of the reaction is limited to twenty to sixty minutes, instead of three to fifteen hours, as employed by these authors.

[With Elmer V. McCollum.]—6-*Thiocyano-2-ethylthiolpyrimidine*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{C(SEt)=N}\\ \mathrm{C(SCN)\cdot CH}\end{array}{>}\mathrm{CH}$, prepared by warming 6-chloro-2-ethylthiolpyrimidine with potassium thiocyanate in acetone or 95% alcoholic solution, crystallises from alcohol in aggregates of rectangular prisms, m. p. 82°. On heating at 80—90° for four to five hours, it is transformed into the thiocarbimido-derivative. This is obtained as a yellow oil, b. p. 200—205°/45—50 mm., which, after some time, deposits a yellow, crystalline compound, m. p. 175—177°. This does not react with ammonia, and is regarded as a polymeric form of 2-ethylthiol-6-thiocarbimidopyrimidine (compare Wheeler and Bristol, *loc. cit.*).

6-*Thiocyano-2-ethylthiol-5-methylpyrimidine*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{C(SEt)=\!=N}\\ \mathrm{C(SCN)\cdot CMe}\end{array}{>}\mathrm{CH}$, crystallises from alcohol in prisms, m. p. 95°. It dissolves in thioacetic acid, forming prismatic crystals, m. p. 179—180°, which probably consist of 6-*thio-2-ethylthiol-5-methylpyrimidine*. 5-*Bromo*-6-*thiocyano*-2-*ethylthiolpyrimidine*,  $\mathrm{N}{<}\begin{array}{l}\mathrm{C(SEt)=\!=N}\\ \mathrm{C(SCN)\cdot CBr}\end{array}{>}\mathrm{CH}$, crystallises from alcohol in prisms, m. p. 81—82°. With thioacetic or thiobenzoic acid, it yields 5-bromo-6-thio-2-ethylthiolpyrimidine, and, when heated for two hours at 150—160°, it is transformed into the thiocarbimido-isomeride.

6-*Oxy*-2-o-*toluidinopyrimidine*,  $\mathrm{NH}{<}\begin{array}{l}\mathrm{C(NH\cdot C_6H_4Me)\colon N}\\ \mathrm{CO\text{————————}CH}\end{array}{>}\mathrm{CH}$, prepared by heating a mixture of 6-oxy-2-ethylthiolpyrimidine and *o*-toluidine for three days on the steam-bath, separates from alcohol or acetic acid in prismatic crystals, m. p. 219—220°. With phosphoryl chloride, it yields 6-*chloro*-2-o-*toluidinopyrimidine*,

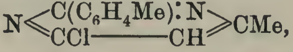


$$\mathrm{N}{<}\begin{matrix}\mathrm{C(NH{\cdot}C_6H_4Me){:}N}\\ \mathrm{CCl\text{———————}CH}\end{matrix}{>}\mathrm{CH},$$

separating from alcohol in crystals, m. p. 78°, which, when heated with alcoholic ammonia, furnishes 6-*amino*-2-o-*toluidinopyrimidine*, crystallising from alcohol in small prisms, m. p. 124°, and when boiled with a benzene solution of aniline gives 6-*anilino*-2-o-*toluidinopyrimidine*, crystallising from alcohol in hexagonal plates, m. p. 128°; the *hydrochloride* forms slender needles, m. p. 126°.

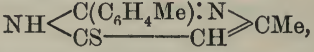
6-*Oxy*-2-p-*toluidinopyrimidine*, prepared from 6-oxy-2-ethylthiolpyrimidine and *p*-toluidine, crystallises from acetic acid in needles, m. p. 270—271°. With phosphoryl chloride, it gives 6-*chloro*-2-p-*toluidinopyrimidine*, separating from alcohol in prisms, m. p. 112—113°. This reacts with aniline, yielding 6-*anilino*-2-p-*toluidinopyrimidine*, which crystallises from alcohol in needles, m. p. 135°; the hydrochloride forms prisms, decomposing at 134°. 6-*Oxy*-2-*β*-*naphthylaminopyrimidine*, prepared from *β*-naphthylamine and 6-oxy-2-ethylthiolpyrimidine, crystallises from alcohol in needles, m. p. 270°.

6-*Chloro*-2-p-*tolyl*-4-*methylpyrimidine*,



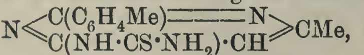
$$\mathrm{N}{<}\begin{matrix}\mathrm{C(C_6H_4Me){:}N}\\ \mathrm{CCl\text{————}CH}\end{matrix}{>}\mathrm{CMe},$$

prepared by heating a mixture of 6-oxy-2-*p*-tolyl-4-methylpyrimidine, phosphorus pentachloride, and phosphoryl chloride, crystallises from alcohol in prisms, m. p. 107°. With potassium thiocyanate, this gives 6-*thiocyano*-2-p-*tolyl*-4-*methylpyrimidine*, separating from alcohol in fern-like crystals, m. p. 123°, which, when warmed with thiobenzoic acid, yields 6-*thio*-2-p-*tolyl*-4-*methylpyrimidine*,



$$\mathrm{NH}{<}\begin{matrix}\mathrm{C(C_6H_4Me){:}N}\\ \mathrm{CS\text{————}CH}\end{matrix}{>}\mathrm{CMe},$$

crystallising from alcohol in slender prisms, m. p. 114°. When the thiocyano-compound is heated for two and a-half hours at 130—135°, it undergoes re-arrangement, yielding prisms, m. p. 207—208°, which probably consist of a polymeric form of the *thiocarbimido*-derivative. With ammonia this gives 6-*thiocarbamido*-2-p-*tolyl*-4-*methylpyrimidine*,



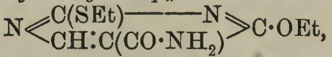
$$\mathrm{N}{<}\begin{matrix}\mathrm{C(C_6H_4Me)\!=\!=\!=\!=\!N}\\ \mathrm{C(NH{\cdot}CS{\cdot}NH_2){\cdot}CH}\end{matrix}{>}\mathrm{CMe},$$

crystallising from alcohol in prisms, m. p. 145—146°. When 6-chloro-2-*p*-tolyl-4-methylpyrimidine is heated with ammonia at 180—190° for two hours, it yields 6-*amino*-2-p-*tolyl*-4-*methylpyrimidine*, separating from alcohol in hexagonal tablets, m. p. 178—179°, and, when warmed with a benzene solution of aniline, 6-*anilino*-2-p-*tolyl*-4-*methylpyrimidine*, crystallising from alcohol in needles, m. p. 120—121°, is obtained; the *hydrochloride* separates from alcohol in clusters of needles, m. p. 269—270° (decomp.).

J. C. C.

Pyrimidines. XXXVI. Synthesis of Cytosine-5-carboxylamide. HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1908, **40**, 233—251. Compare Abstr., 1907, i, 559, 1083).—The authors have previously shown that ethyl-*ψ*-thiocarbamide and ethyl ethoxymethylenemalonate condense to form ethyl 2-ethylthiol-6-oxypyrimidine-5-carboxylate, and that the corresponding acid is readily obtained from this. They have now succeeded in greatly increasing the yield of pyrimidine in this condensation, and have made it the starting point for further syntheses.

The *acid chloride* of 6-*chloro*-2-*ethylthiolpyrimidine*-5-*carboxylic acid*, $\mathrm{N}\left<\begin{matrix}\mathrm{C(SEt)\text{——}N}\\ \mathrm{CH{:}C(COCl)}\end{matrix}\right>\mathrm{CCl}$, prepared by boiling the dry oxy-acid with phosphoryl chloride, separates from light petroleum in radiating clusters of colourless prisms, m. p. 38—40°. With cold aqueous ammonia, the corresponding *amide*, $\mathrm{N}\left<\begin{matrix}\mathrm{C(SEt)\text{———}N}\\ \mathrm{CH{:}C(CO{\cdot}NH_2)}\end{matrix}\right>\mathrm{CCl}$, is formed, which separates from benzene in long, hair-like crystals, m. p. 134°, and with sodium ethoxide yields 6-*ethoxy*-2-*ethylthiolpyrimidine*-5-*carboxylamide*,

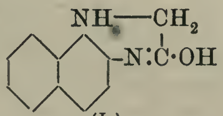


$$\mathrm{N}\left<\begin{matrix}\mathrm{C(SEt)\text{———}N}\\ \mathrm{CH{:}C(CO{\cdot}NH_2)}\end{matrix}\right>\mathrm{C{\cdot}OEt},$$

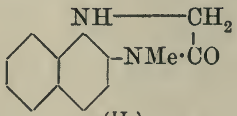
m. p. 134°. When the acid chloride of 6-chloro-2-ethylthiolpyrimidine-5-carboxylic acid is warmed with aqueous ammonia, 6-*amino*-2-*ethylthiolpyrimidine*-5-*carboxylamide*, $\mathrm{N}\left<\begin{matrix}\mathrm{C(SEt)\text{———}N}\\ \mathrm{CH{:}C(CO{\cdot}NH_2)}\end{matrix}\right>\mathrm{C{\cdot}NH_2}$, stout prisms, m. p. 218—219°, is produced; with bromine, it yields a *dibromo*-additive compound. When the latter is heated until the loss corresponds with the weight of one molecular proportion of hydrogen bromide, the resulting material dissolved in dilute potassium hydroxide, and the solution acidified with acetic acid, *cytosine*-5-*carboxylamide*, $\mathrm{N}\left<\begin{matrix}\mathrm{CO\text{—————}NH}\\ \mathrm{C(NH_2){\cdot}C(CO{\cdot}NH_2)}\end{matrix}\right>\mathrm{CH}$, is obtained. This is also formed, together with the acid, by the action of hydrochloric acid on 6-amino-2-ethylthiolpyrimidine-5-carboxylamide; it does not melt at 310°. The substance previously regarded as having this constitution (*loc. cit.*, 1083) was probably impure or partly hydrated cytosine. On hydrolysis with hydrochloric acid, it yields cytosine-5-carboxylic acid, and it forms the following salts: *hydrochloride*, colourless, stout, pointed prisms; *nitrate*, truncated octahedrons or tufts of short hairs; *sulphate*, pearly scales; and *picrate*. J. C. C.

Preparation of 2-Hydroxydihydro- and 1-Alkyl-2-ketodihydro-quinoxalines. MARTIN LANGE (D.R.-P. 196563).—The *o*-nitrosophenols interact with aldehydes and primary amines or with Schiff's bases to form quinoxaline derivatives.

2-*Hydroxydihydro*-1′ : 2′-*naphthaquinoxaline* (I), a yellow, sandy



(I.)



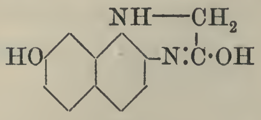
(II.)

powder, m. p. 240°, is produced by adding acetaldehyde and ammonium chloride to an alkaline solution of 1-nitroso-β-naphthol.

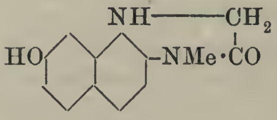
2-*Keto*-1-*methyldihydro*-1′ : 2′-*naphthaquinoxaline* (II), m. p. 155·5°, is obtained by substituting methylamine hydrochloride for ammonium chloride in the foregoing reaction. The corresponding 2-keto-1-ethyldihydro-1′ : 2′-naphthaquinoxaline, m. p. 164°, is produced by condensing 1-nitroso-β-naphthol with 30% ethylamine and acetaldehyde.

The patent contains a description of several other quinoxalines derived from 1-nitroso-β-naphthol, 2-nitroso-α-naphthol, and their carboxylic and sulphonic acids, and, in addition, two obtained from nitroso-2 : 7-dihydroxynaphthalene and one from dinitrosoresorcinol.

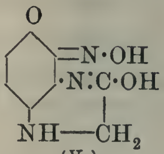
These compounds have the formulæ:



(III.)



(IV.)



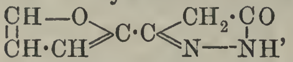
(V.)

(III) and (IV) are obtained from 2 : 7-dihydroxynaphthalene, acetaldehyde, and ammonia, or methylamine, respectively.

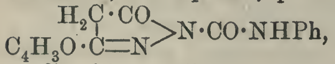
(V), which is produced from dinitrosoresorcinol, acetaldehyde, and ammonia, separates in orange crystals. G. T. M.

Ethyl Pyromucylacetate [Furfuroylacetate]. II. 3-Furyl-5-pyrazolone. Henry A. Torrey and Joaquin E. Zanetti (*J. Amer. Chem. Soc.*, 1908, 30, 1241—1244).—When ethyl furfuroylacetate is treated with phenylhydrazine, it is converted into 1-phenyl-3-furyl-5-pyrazolone. This compound and some of its derivatives have been described previously (Abstr., 1907, i, 146).

By the action of hydrazine on ethyl furfuroylacetate, 3-*furyl-5-pyrazolone*,



$\begin{matrix}CH-O\\ \|\\ CH\cdot CH\end{matrix}\!\!>C\cdot C<\!\!\begin{matrix}CH_2\cdot CO\\ |\\ N-NH\end{matrix}$, m. p. 223° (decomp.), is obtained, and forms small, rectangular plates. The *picrate* decomposes at 192°. The *acetyl* derivative, m. p. 153—154°, and the *diacetyl* derivative, m. p. 102°, crystallise in long, white needles. The *benzylidene* derivative forms a light brown, amorphous powder, and does not melt at 300°. When the pyrazolone is treated with phenylcarbimide, a compound, probably 3-*furyl*-5-*pyrazolonephenylcarbamide*,



$\begin{matrix}H_2C\cdot CO\\ |\\ C_4H_3O\cdot C{=}N\end{matrix}\!\!>N\cdot CO\cdot NHPh$, m. p. 192°, is obtained in the form of small, white needles. E. G.

Trihydroxymethyldihydrouracil. Robert Behrend and Karl Beer (*Annalen*, 1908, 362, 115—122. Compare Behrend and Grünewald, Abstr., 1902, i, 834).—A further account of the properties of α- and β-trihydroxymethyldihydrouracils (compare Behrend and Osten, Abstr., 1906, i, 309). Both of these compounds crystallise with $1H_2O$. The compound obtained by the interaction of the β-compound and phenylhydrazine is a *phenylhydrazide*, $C_{11}H_{14}O_4N_4$, since it liberates phenylhydrazine when treated with alkali. Both α- and β-trihydroxymethyldihydrouracils are oxidised by potassium permanganate in the presence of potassium hydrogen carbonate, yielding *potassium acetoxalurate*, $C_5H_5O_5N_2K,2H_2O$, crystallising in needles decomposing at 214—216°. An *acid* salt, $C_5H_5O_5N_2K,C_5H_6O_5N_2$, m. p. 201°, separates when a solution of the neutral salt is acidified with hydrochloric acid.

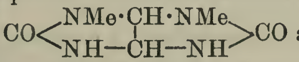
The α-uracil when heated at 105—110° loses $2H_2O$, yielding a yellow powder which decomposes at 140—145°. The β-uracil also loses $2H_2O$ at 105—110°, yielding a syrupy acetylallanturic acid. The same acid is also formed when a neutral or slightly alkaline aqueous solution of either the α- or β-uracil is warmed. A *phenylhydrazone*, $C_{11}H_{12}O_3N_4$, forming yellow crystals decomposing at 219—220°, was prepared.

Acetylallanturic acid is oxidised by potassium permanganate in the presence of potassium hydrogen carbonate to oxaluric acid and acetic acid; in no case was either acetoxaluric acid or acetylcarbamide formed.

W. H. G.

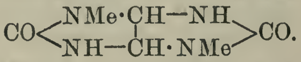
Dimethylglycoluril and β-Methylhydantoin. Emil Weitzner (*Annalen*, 1908, **362**, 125—131).—An account of attempts to obtain a fruitful and simple method for preparing β-methylhydantoin.

Methylcarbamide, or, better, its acetyl derivative, reacts with glyoxal in aqueous solution in the presence of hydrochloric acid, yielding dimethylglycoluril (compare Franchimont and Klobbie, Abstr., 1888, 1179). The product so formed is shown to be a mixture of the two isomerides:



$$CO<\begin{matrix}NMe\cdot CH\cdot NMe\\ NH—CH—NH\end{matrix}>CO$$

and



$$CO<\begin{matrix}NMe\cdot CH—NH\\ NH—CH\cdot NMe\end{matrix}>CO.$$

Both these compounds when decomposed with hydrochloric acid yield the same product, namely, a mixture of α- and β-methylhydantoins, which is separated only with great difficulty. The best method for obtaining β-methylhydantoin is by acting on sarcosine hydrochloride with potassium cyanate in aqueous solution, and heating the resulting solution with hydrochloric acid.

The mixture of isomeric *dimethylglycolurils* prepared from glyoxal and acetylmethylcarbamide may be separated by fractional crystallisation from water. Both isomerides crystallise in long, colourless needles, and melt at 285—287° and 230—232° respectively.

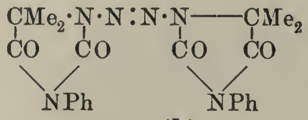
W. H. G.

Preparation of Azoxy-derivatives. O. Dieffenbach (D.R.-P 197714).—Azoxy-compounds may be conveniently obtained free from amines by digesting a mixture of a nitro-compound and hydrazo-derivative until they have interacted to furnish a mixture of azo- and azoxy-derivatives.

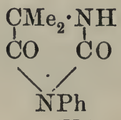
A mixture of azo- and azoxy-*o*-toluene is thus produced by maintaining a mixture of *o*-nitrotoluene, hydrazo-*o*-toluene, toluene, and aqueous sodium hydroxide (10%) at 90° for eight hours. Under similar conditions a mixture of *o*-nitrobenzoic acid and hydrazobenzene yields sodium *o*-azoxybenzoate and azobenzene, which are readily separated. This reaction may be combined advantageously with the electrolytic production of hydrazo-derivatives.

The azoxy-compound is reduced electrolytically to a hydrazo-compound and then more nitro-compound is added, which is then reduced to the azoxy-compound by the hydrazo-derivative present, so that the nitro-compound is being continuously reduced chemically whilst the electrolytic reduction is effected on the azoxy-derivative. G. T. M.

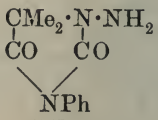
Hydantointetrazones. J. R. BAILEY (*J. Amer. Chem. Soc.*, 1908, 30, 1412—1418. Compare Abstr., 1904, i, 826).—The author adduces further evidence in favour of the constitution of the azohydantoins (*loc. cit.*) by showing the relation of azophenyldimethylhydantoin (I) to phenyldimethylhydantoin (II) and to aminophenyldimethylhydantoin (III).



(I.)



(II.)



(III.)

1-Azo-3-phenyl-5 : 5-dimethylhydantoin after purification by crystallisation from ethyl acetoacetate decomposes at 285° (corr.), instead of 270° as given previously. When heated at 60° with sulphuric acid or boiled with alcoholic potash, it loses nitrogen and yields 3-*phenyl*-5 : 5-*dimethylhydantoin*, crystallising from water in prisms, m. p. 171° (corr.), which is also obtained by condensing phenylcarbimide with amino*iso*butyronitrile and hydrolysing the product.

[With BARNEY BROOKS.]—1-*Amino*-3-*phenyl*-5 : 5-*dimethylhydantoin*, m. p. 154·5° (corr.), is prepared by the action of dilute sulphuric acid on 1-carboxy*iso*propylamino-3-phenyl-5 : 5-dimethylhydantoin. It is oxidised with bromine water to 1-azo-3-phenyl-5 : 5-dimethylhydantoin. 1-*Benzylideneamino*-3-*phenyl*-5 : 5-*dimethylhydantoin*, prepared by heating aminophenyldimethylhydantoin with benzaldehyde or by heating phenylcarbimide with the benzylidenehydrazone of hydrazino*iso*butyric acid, crystallises from alcohol in long, slender, pale yellow needles, m. p. 154° (corr.). J. C. C.

[Preparation of Diazo-derivatives of 1-Amino-β-naphtholsulphonic Acids.] KALLE & Co. (D.R.-P. 195228 and 195322).—On adding aqueous sodium nitrite to a mixture of 1-amino-β-naphthol-4-sulphonic acid, zinc sulphate, and zinc hydroxide, diazotisation sets in, and is completed by heating at 40—55° for one or two hours. The diazo-derivative may be precipitated by the addition of acetic acid and sodium chloride. Other sulphonic acids of 1-amino-β-naphthol or 2-amino-α-naphthol may be diazotised in a similar manner.

The zinc salt may be replaced by the salts of magnesium, cobalt, nickel, and manganese, and, in general, by metallic salts of neutral reaction which are highly dissociated in aqueous solution. G. T. M.

The Extractives of Muscular Tissue. Relationship of Oblitine to Carnitine. R. KRIMBERG (*Zeitsch. physiol. Chem.*, 1908, 56, 417—424. Compare this vol., ii, 609).—When carnitine is evaporated several times with 96% alcohol and a little hydrochloric acid, a product is formed from which oblitine can be isolated in the form of its hydrochloride. Oblitine would thus appear to be the diethyl ester of dicarnitine. The platinichloride has the formula $C_{18}H_{38}O_5N_2Cl_6Pt$, and not $C_{18}H_{40}O_5N_2Cl_6Pt$ (Kutscher). Since Kutscher in the isolation of oblitine used methods which would transform carnitine into oblitine, it is questionable whether this latter exists in muscle extract.

J. J. S.

Blood-pigment. IX. Leon Marchlewski (*Zeitsch. physiol. Chem.*, 1908, **56**, 316—320. Compare this vol., i, 232).—A further investigation of the action of diazobenzene chloride on hæmopyrrole has shown that at least four, and probably five, products are formed. (*a*) A product, the hydrochloride of which crystallises in brown, monoclinic or triclinic needles, m. p. 233°. (*b*) Rhombic crystals, with a ruby-red colour and coppery lustre, m. p. 268°. (*c*) Green needles of a hydrochloride, m. p. above 300°. (*d*) Brown needles with a green shimmer of a hydrochloride, m. p. 185—186°. The chief product is usually (*a*); product (*d*) appears to be formed when the conditions are somewhat altered.

It is shown that treatment of hæmopyrrole with acid affects it in such a manner that the yield of product (*a*) is diminished, and is ultimately nil. J. J. S.

Part Played by Alkali in the Hydrolysis of Proteins by Trypsin. T. Brailsford Robertson and C. L. A. Schmidt (*J. Biol. Chem.*, 1908, **5**, 31—48).—The change in alkalinity during tryptic fermentation has been followed by means of the gas chain. It is found that when the total hydroxyl-ion concentration is greater than 10^{-6}, the changes in concentration can be expressed by a unimolecular formula, but that with lower concentrations the change can be represented by a bimolecular formula. These facts appear to be inconsistent with the view that the hydroxyl ions act as an accessory catalyst, but are in harmony with the view that the real catalyst is a hydrolysable compound of trypsin with sodium hydroxide or other base present in the system.

It is suggested that the equilibrium, as regards change in $\overline{OH}$ concentrations, which is attained after some time is a "false" equilibrium depending on the sum of the relations between the protein, trypsin, and alkali. The proteins used were casein and protamine.

J. J. S.

Hydrolysis of Legumin from the Vetch. Thomas B. Osborne and Frederick W. Heyl (*Amer. J. Physiol.*, 1908, **22**, 423—432).—The general properties of vetch legumin are similar to those of the pea legumin described previously (Abstr., 1907, i, 806). On hydrolysis, the various amino-acids are found in somewhat different proportions; these differences are most marked in the case of valine, aspartic acid, and lysine, but some hesitation is felt in drawing conclusions that these are sufficient in the present state of our technique to warrant the assertion that the two proteins are different. W. D. H.

Photomethæmoglobin. Otto Leers (*Biochem. Zeitsch.*, 1908, **12**, 252—258).—When methæmoglobin solutions are exposed to sunlight, the brown colour is, as Bock has shown, converted into a red colour, and the modification of the blood-pigment, termed photomethæmoglobin, is formed. Its spectrum shows great similarity with that of cyanohæmoglobin. Methæmoglobin was prepared by a variety of methods, and this was converted into photomethæmoglobin by treatment with potassium ferricyanide and exposure to sunlight. The same effect was also produced by sodium ferro- and ferri-cyanides and other cyano-compounds. The solutions thus obtained exhibit on concentration the characteristic hydrocyanic acid odour, and give also the Prussian-blue and other characteristic hydrocyanic acid tests. Other evidence was also adduced to indicate the formation of hydrocyanic acid in the methæmoglobin solutions when treated with potassium ferricyanide; the facts indicate that photomethæmoglobin and cyano-(met)hæmoglobin are identical modifications of the blood-pigment.

S. B. S.

Coaguloses. III. D. Lawroff (*Zeitsch. physiol. Chem.*, 1908, **56**, 343—362. Compare Abstr., 1907, i, 995).—The present experiments were performed with crystallised egg-albumin, and confirm those previously recorded with hæmoglobin and caseinogen. In the various fractions the same two types of coagulose-yielding substances were detected after relatively short peptic digestion. W. D. H.

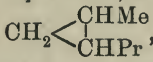
Organic Chemistry.

Syntheses of Methane by means of Calcium Hydride. M. Mayer and V. Altmayer (*Ber.*, 1908, **41**, 3074—3080. Compare Abstr., 1907, i, 457).—Methane can be synthesised by the action of carbon, its monoxide, or dioxide on freshly-prepared calcium hydride. With carbon monoxide the reaction begins at 400°, and is rapid at 500°; thus when the gas is passed at the rate of 0·5 c.c. per minute the issuing mixture contains 42·75% methane and 51·86% hydrogen, and when the rate is 1 c.c. per minute the product contains over 60% of methane. At higher temperatures the amount of methane tends to decrease. The reaction can probably be represented by the equations: $3CaH_2 + 3CO = CH_4 + 3CaO + 2C + H_2$ and $CaH_2 + 2C = CaC_2 + H_2$. Calcium carbide, calcium oxide, and carbon have been found in the residue. Carbon dioxide behaves in much the same manner as the monoxide.

With carbon (lamp-black) and calcium hydride, hydrogen is produced at 270°, and the formation of methane can only be recognised at higher temperatures. At 500° the gaseous mixture contains about 40% of methane. J. J. S.

Studies in the Hexene and Heptene Series. Nicolai D. Zelinsky and E. S. Prschevalsky (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1105—1123).—The action of quinoline or of aqueous or alcoholic potassium hydroxide on *n*-hexyl iodide yields as main fraction a *hydrocarbon*, C_6H_{12}, b. p. 64—64·5°, D_4^{15} 0·6789, D_4^{20} 0·6750, $n^{18·5}$ 1·3896, which gives only valeric acid on oxidation; the authors regard it as *n*-hexylene.

β-Methylhexyl iodide, $C_4H_9·CHMe·CH_2I$, prepared from the corresponding alcohol by the action of iodine and phosphorus, has b. p. 78—79°/19 mm., D_4^{17} 1·3707, D_4^{21} 1·3663, n^{21} 1·4891.

*Methylpropyl*cyclo*propane*,  $CH_2<\begin{matrix}CHMe\\ |\\ CHPr\end{matrix}$, obtained by the action of alcoholic potassium hydroxide on β-methylhexyl iodide, b. p. 92—92·5°/753 mm., D_4^{15} 0·7077, D_4^{20} 0·7033, n^{18} 1·4044, gives, on oxidation with permanganate, (1) methyl *n*-butyl ketone; (2) butyric acid; (3) valeric acid; (4) heptoic or *iso*heptoic acid; (5) a glycol, $C_7H_{16}O_2$, possibly $CH_2Pr·CMe(OH)·CH_2·OH$, which, on further oxidation, gives butyric, valeric (?), and heptoic or *iso*heptoic acid. On adding hydrogen iodide to methylpropyl*cyclo*propane and treating the resulting iodo-compound with dilute aqueous potassium hydroxide in a sealed tube at 100—105°, Δ^{γ}-*heptylene*, CHEt:CHPr, b. p. 94·5—95·5°/757 mm., D_4^{15} 0·7124, D_4^{20} 0·7083, $n^{21·5}$ 1·4077, is obtained; on oxidation with permanganate, this hydrocarbon yields butyric and propionic acids, together with traces of acetone and valeric acid.

T. H. P.

Ozonides of the Simple Olefines. CARL D. HARRIES and KARL HAEFFNER (*Ber.*, 1908, 41, 3098—3102).—Although amylene and hexylene ignite when brought into contact with ozone, nevertheless it has been found possible to prepare their ozonides by using the method of Harries and Tank (this vol., i, 517), namely, treating a very dilute solution of the substance in an indifferent solvent with ozone. The ozonides of these olefines are very stable substances, and may be distilled in a vacuum. It is probable, from the observed values of the molecular refraction and dispersion of these ozonides, that the molecule contains one carbonyl oxygen atom and two ether oxygen atoms.

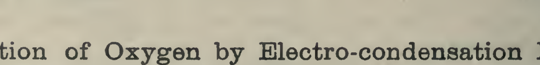
Amylene ozonide (*trimethylethylene ozonide*), $C_5H_{10}O_3$, is prepared by passing ozone into a dilute solution of the olefine in hexane, and heating at 60° in a vacuum the crude ozonide obtained after distilling off the solvent; it is a limpid, colourless liquid. The *ozonide* obtained by treating the crude ozonide with an aqueous solution of sodium hydrogen carbonate, when analysed, gives values which lie between those required for $C_5H_{10}O_3$ and $C_5H_{10}O_4$; it is far more explosive than the normal ozonide.

Hexylene ozonide, $C_6H_{12}O_3$, is prepared in the same way as the amylene ozonide. The crude ozonide first obtained is viscid, but yields the normal ozonide, a limpid liquid, when distilled at 60° under 12 mm. pressure. The amylene and hexylene ozonides are not readily decomposed by water.

Propylene ozonide is obtained by passing ozone into a dilute solution of propylene in ethyl chloride cooled in a carbon dioxide-ether freezing mixture. It is a limpid liquid with a pungent odour, b. p. 29—30°/19·5 mm., becomes solid at low temperatures, explodes with great violence when heated in a test-tube, and is rapidly decomposed by water. W. H. G.

Absorption of Oxygen by Electro-condensation Products. SIMA M. LOSANITSCH (*Monatsh.*, 1908, 29, 753—762).—Chiefly an account of work already published (Abstr., 1897, i, 179; this vol., ii, 32), and a criticism of Jovitschitsch's work (this vol., i, 118).

Since the compound $(C_{12}H_{22}O)_2$, formed by absorption of oxygen by the electro-condensation product of ethylene, distils unchanged, the oxygen must be in chemical combination. The addition may take place at the ethylene linkings in one of the two manners:



$$\cdot CO\cdot CH_2\cdot \longleftarrow \cdot CH{:}CH\cdot \longrightarrow \cdot CH\!<\!\begin{matrix}CH\cdot\\ |\\ O\end{matrix}.$$

The solid condensation product of acetylene, when treated with ozonised oxygen, forms a *compound*, $(C_6H_8O_2)_n$; the liquid condensation product, on the other hand, absorbs oxygen only slowly, and, after several months, contains less oxygen than required for the formula $(C_6H_{10}O)_2$. Both condensation products of acetylene with ethylene absorb oxygen, but without forming definite compounds. The oxygenated compound derived from acetylene and carbon monoxide absorbs more oxygen than previously stated, but still without reaching the composition $(C_8H_8\cdot CO\cdot O_2)_n$. G. Y.

Action of Organo-magnesium Compounds on Crotonaldehyde and the Optical Behaviour of the Products. JOHANN REIF (*Ber.*, 1908, 41, 2739—2746).—The paper is a continuation of Grignard's research on the action of magnesium methyl iodide or magnesium *iso*amyl bromide on crotonaldehyde (Abstr., 1901, i, 679). Employing the same method, the author has examined the action of magnesium ethyl, propyl, *iso*propyl, and *iso*butyl bromides. The resulting unsaturated alcohols, CHMe:CH·CH(OH)·CH_2R, described below are colourless, mobile liquids, which exhibit a normal molecular refraction, are oxidised by 1% potassium permanganate to the corresponding glycerols, and by distillation with potassium hydrogen sulphate yield diolefines of the type CHMe:CH·CH:CHR, which, in agreement with Brühl's observations on substances containing the group >C:CH·CH:C<, exhibit a marked exaltation of the molecular refraction.

The following new compounds are mentioned:

Δ^{β}-Pentene-δ-ol yields a *chloride*, CHMe:CH·CHMeCl, b. p. 103—106° (decomp.), and a *glycerol*, $C_5H_{12}O_3$, b. p. 244—246°, of which the *triacetate* has m. p. 121° and b. p. 241—243°. *Δ^{β}-Hexene-δ-ol*, CHMe:CH·CHEt·OH, b. p. 133—135° or 85—87°/118 mm., D_4^{25} 0·8409, n_D^{25} 1·4312; the *acetate* has b. p. 153—155°; the *chloride* has b. p. 122—126° (decomp.) or 65—70°/110 mm., and is converted by methyl-alcoholic potassium hydroxide into *δ-methoxy-Δ^{β}-hexene*, CHMe:CH·CHEt·OMe, b. p. 110—113° (compare Vaubel, Abstr., 1891, 996); the *glycerol*, $\beta\gamma\delta$-hexantriol, has b. p. 256—257°, and yields a solid *triacetate*, b. p. 254—256°. *Δ^{β}-Heptene-δ-ol*,

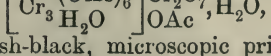
CHMe:CH·$CHPr^{\alpha}$·OH,

b. p. 152—154° or 104—105°/106 mm., D_4^{20} 0·8445, n_D^{20} 1·4373, forms an *acetate*, b. p. 168—170°, and a *chloride*, b. p. 140—144° or 86—90°/104 mm. *ζ-Methyl-Δ^{β}-hexene-δ-ol*, CHMe:CH·$CHPr^{\beta}$·OH, has b. p. 139—140° or 92—94°/105 mm., D_4^{20} 0·8426, n_D^{20} 1·438; the *acetate* has b. p. 108—110°/100 mm. *ζ-Methyl-Δ^{β}-heptene-δ-ol*,

CHMe:CH·CH(OH)·CH_2·$CHMe_2$,

D_4^{19} 0·8389, n_D^{19} 1·4395, forms an *acetate*, b. p. 123—126°/108 mm. *$\Delta^{\beta\delta}$-Pentadiene*, C_5H_8, b. p. 40—41°, D_4^{25} 0·6794, n_D^{25} 1·4206. *$\Delta^{\beta\delta}$-Hexadiene*, C_6H_{10}, b. p. 80—82°, D_4^{21} 0·7177, n_D^{21} 1·4463, yields a *dihydrobromide*, b. p. 199—201° or 98—102°/30 mm., and a *tetrabromide*, m. p. 180°. *$\Delta^{\beta\delta}$-Heptadiene*, C_7H_{12}, b. p. 104—106°, $D_4^{21\cdot5}$ 0·7327, $n_D^{21\cdot5}$ 1·4486. *ϵ-Methyl-$\Delta^{\beta\delta}$-hexadiene*, C_7H_{12}, b. p. 97—99°, $D_4^{24\cdot5}$ 0·7192, $n_D^{24\cdot5}$ 1·4266. *ζ-Methyl-Δ-$^{\beta\delta}$-heptadiene*, C_8H_{14}, b. p. 114—116°, D_4^{25} 0·7401, n_D^{25} 1·4397. *η-Methyl-$\Delta^{\beta\delta}$-octadiene*, C_9H_{16}, b. p. 149°, D_4^{18} 0·7521, n_D^{18} 1·4543, yields a *dihydrobromide*, b. p. 124—126°/16 mm., and a *tetrabromide*, b. p. 184°/18 mm. C. S.

Salts of an Acetatochromo-base. RUDOLF F. WEINLAND (*Ber.*, 1908, 41, 3236—3245).—When chromic acid (1 part) is warmed at 100° with glacial acetic acid (2 parts) until no more carbon dioxide is evolved, the *dichromate acetate* of an acetatochromo-base,



$$\left[Cr_3\begin{matrix}(OAc)_6\\H_2O\end{matrix}\right]\begin{matrix}Cr_2O_7\\OAc\end{matrix},H_2O,$$

is obtained in brownish-black, microscopic prisms. If this salt is treated with a little water, it first dissolves, and afterwards olive-green plates of a *chromate acetate* with 1·5 mols. of chromic acid,

$$\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{H_2O}\end{matrix}\right]\begin{matrix}\frac{1}{2}\mathrm{Cr_2O_7}\\ \frac{1}{2}\mathrm{CrO_4}\\ \mathrm{OAc}\end{matrix},1\tfrac{1}{2}\mathrm{H_2O}$$

are precipitated. On the other hand, if the dichromate acetate is recrystallised from a larger quantity of water, dark green crystals of a simpler *chromate acetate*, $\left[\mathrm{Cr_3}\begin{matrix}\mathrm{(OAc)_6}\\ \mathrm{H_2O}\end{matrix}\right]\begin{matrix}\mathrm{CrO_4}\\ \mathrm{OAc}\end{matrix},3\frac{1}{2}\mathrm{H_2O}$, are produced. This compound is also formed directly from the two acids.

Addition of hydrochloric acid to a solution of the dichromate acetate causes the separation of a *chloride chromate*,

$$\left[\mathrm{Cr_3\,(OAc)_6}\right]\begin{matrix}\mathrm{Cl}\\ \mathrm{CrO_4}\end{matrix},4\mathrm{H_2O},$$

as dark green crystals.

The *platinichloride*, $\left[\mathrm{Cr_3\,(OAc)_6}\right]\begin{matrix}\mathrm{(OH)_2}\\ \frac{1}{2}\mathrm{PtCl_6}\end{matrix},5\mathrm{H_2O}$, is obtained from all the above salts of the base.

A basic *chromate acetate*, $\left[\mathrm{Cr_3(OAc)_6}\right]\begin{matrix}\mathrm{OH}\\ \frac{1}{2}\mathrm{CrO_4}\\ \mathrm{OAc}\end{matrix},5\mathrm{H_2O}$, is obtained when lead acetate is added to the dichromate acetate until only $\frac{1}{4}$ mol. of chromic acid is left in the solution, and a basic *chloride*,

$$\left[\mathrm{Cr_3\,(OAc)_6}\right]\begin{matrix}\mathrm{OH}\\ \mathrm{Cl}\\ \mathrm{OAc}\end{matrix},5\mathrm{H_2O},$$

and basic *nitrate*, $\left[\mathrm{Cr_3\,(OAc)_6}\right]\begin{matrix}\mathrm{OH}\\ \mathrm{NO_3}\\ \mathrm{OAc}\end{matrix},2\frac{1}{2}\mathrm{H_2O}$, can be obtained by similar means. The *diacetate*, $\left[\mathrm{Cr_3\,(OAc)_6}\right]\begin{matrix}\mathrm{OH}\\ \mathrm{(OAc)_2}\end{matrix},5\mathrm{H_2O}$, is obtained from the solution of the chromate acetate, after treatment with lead acetate, as a light green, crystalline powder. Silver nitrate precipitates silver acetate from its concentrated solution, proving the presence of acetic acid ions, but the nitrate acetate solution gives no such precipitate. The method of preparation of these compounds shows that the positive complex contains three atoms of chromium and six acetic residues. The water remaining after drying to constant weight in a vacuum over sulphuric acid is held to be joined to the cation.

The free acetatochromo-base prepared from the chloride acetate and excess of silver oxide is dark green in solution. The alkaline liquid is unstable, and gradually becomes acid.

The corresponding *iron base*, $\left[\mathrm{Fe_3(OAc)_6}\right]\begin{matrix}\mathrm{Cr_2O_7}\\ \mathrm{OAc}\end{matrix},\mathrm{H_2O}$, and propionato-bases have been prepared. W. R.

Stereochemical Nature of the Addition of Chlorine to Crotonic Acid. ARTHUR MICHAEL and O. D. E. BUNGE (*Ber.*, 1908, 41, 2907—2913).—Ordinary fumaroid crotonic acid absorbs chlorine both in the dark and in sunlight, forming $\alpha\beta$-dichlorobutyric acid, m. p. 63°, and the same compound is obtained under similar conditions from *allo*crotonic acid. A stereoisomeric dichlorobutyric acid, m. p. 78°, is produced by the addition of hydrogen chloride to α-chlorocrotonic acid, and is regarded as the maleoid derivative. That this is not the case is shown by the fact that the more fusible dichlorobutyric acid has a greater electrical conductivity than the isomeride, and it must therefore be regarded as the maleoid derivative (crotonic acid *allo*dichloride). The fumaroid acid yields, primarily, maleoid additive products, and the further isomeric change takes place much less readily in the case of the crotonic acids than with the cinnamic acids. Actinic rays are unable to effect it, and it requires prolonged heating with concentrated hydrochloric acid to bring about the conversion of crotonic acid *allo*dichloride into the less fusible isomeride.

Of the two dichlorosuccinic acids melting at 175° and 215°, the more fusible isomeride is the stronger acid. E. F. A.

Action of Ozone on Compounds containing Double and Treble Linkings. Ettore Molinari (*Ber.*, 1908, **41**, 2782—2785).—The author replies to Harries' criticisms (this vol., i, 387), and re-states his right to work on ozonides. C. S.

Triolein Ozonide and its Decomposition Products. Ettore Molinari and P. Fenaroli (*Ber.*, 1908, **41**, 2789—2794).—When triolein is ozonised in hexane solution, an insoluble, gelatinous, yellow mass, probably a polymerised ozonide, is obtained, which is converted by thirty minutes' heating with 1% potassium hydroxide on the water-bath into *triolein ozonide*, $C_{57}H_{104}O_{15}$, a viscous, colourless oil, which decomposes at 136°. This ozonide, not the polymerised form, is obtained by the ozonisation of olive oil. It is decomposed by 30% alcoholic potassium hydroxide on the water-bath, yielding glycerol, azelaic and nonoic acids, a white hydroxy-acid, $C_{18}H_{36}O_3$ (compare Molinari and Soncini, Abstr., 1906, i, 792), and an oily *acid*, $C_{18}H_{32}O_6$, which is oxidised quantitatively to azelaic acid by potassium permanganate. Hydrogen peroxide is not formed, and aldehydes only in small amount.

Arnold and Mentzel's benzidine reaction is the best test for hydrogen peroxide in the presence of aldehydes; some of the higher aldehydes give with potassium ferricyanide and ferric chloride, or with titanium sulphate, the same reactions as hydrogen peroxide.

The authors hope that the saponification value of ozonides will form a new constant in the analysis of oils and fats. C. S.

Products of the Decomposition of Oleic Acid Ozonide. Ettore Molinari and C. Barosi (*Ber.*, 1908, **41**, 2794—2799).—According to Harries, the primary products of the decomposition of oleic acid ozonide by hot water are exclusively hydrogen peroxide, nonaldehyde, and the semialdehyde of azelaic acid (Abstr., 1906, i, 793; 1907, i, 11); Molinari and Soncini (Abstr., 1906, i, 792; compare also preceding abstract) obtained no hydrogen peroxide, but aldehydes in small amount, and mainly azelaic, nonoic, and two other acids, $C_{18}H_{32}O_6$ and $C_{18}H_{36}O_3$. To ascertain whether these four acids are secondary oxidation products, the authors have investigated the decomposition of oleic acid ozonide, D^{18} 1·0218, by hot saturated potassium hydrogen sulphite. The reaction is very complicated, and several of the products have not yet been investigated. The main results are: (*a*) primarily formed acids are azelaic, nonoic, and the acids $C_{18}H_{32}O_6$ and $C_{18}H_{36}O_3$. The acid $C_{18}H_{36}O_3$ (calcium salt insoluble) has m. p. 41° (compare Molinari and Soncini, *loc. cit.*), and is a hydroxystearic acid, $CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot[CH_2]_8\cdot CO_2H$, produced by the aldol condensation of nonaldehyde and nonoic acid. The acid $C_{18}H_{32}O_6$ (calcium salt soluble) is probably produced by the condensation of 2 mols. of the semialdehyde of azelaic acid; (*b*) the aldehydes liberated from their bisulphite compounds undergo polymerisation; *paranonaldehyde*, $(C_9H_{18}O)_3$, a white, crystalline mass, m. p. 28°, has been isolated, and also another substance, b. p. 190°, which forms a *semicarbazone*, $C_{19}H_{39}O_2N_3$, m. p. 54°, and probably is formed by the aldol condensation of 2 mols. of nonaldehyde; (*c*) the semialdehydes are isolated in the form of a viscous, brown oil, which no longer shows the properties of aldehydes, and consists probably of condensation or oxidation products of the semialdehyde of azelaic acid. By prolonged boiling with water, azelaic acid is extracted, and the residue contains the acid $C_{18}H_{32}O_6$ and other unexamined substances. C. S.

Constitution of the So-called Elæomargaric Acid. TOKUHEI KAMETAKA (*J. Coll. Sci. Tōkyō*, 1908, **25**, iii, 1—8. Compare Trans., 1903, **83**, 1042).—Elæomargaric acid cannot be a homologue of sorbic acid, as stated by Cloez (this Journ., 1877, i, 454), since it does not yield tartaric acid when oxidised with potassium permanganate (compare Doebner, Abstr., 1890, 1274). Cloez also states that it is a homologue of stearolic acid, but this is improbable, since it does not give a definite product with concentrated sulphuric acid. As stated by Maquenne (Abstr., 1903, i, 62), elæomargaric acid when oxidised yields azelaic acid, but the presence of valeric acid could not be established. It is therefore highly probable that one of the two ethylene linkings in elæomargaric acid is in the middle of the chain of eighteen carbon atoms. The other ethylene linking is probably situated on that side of the middle ethylene linking which is further removed from the carboxyl group. This view is supported by the behaviour of the acid towards aniline; it yields an *anilide*, $C_{18}H_{31}O\cdot NHPh$, which crystallises in lustrous scales, m. p. about 80°, but does not form an aniline additive product; consequently, an ethylene linking is not near the carboxyl group (compare Autenrieth and Pretzell, Abstr., 1903, i, 474). The anilide combines with bromine, forming a *substance*, m. p. about 95°.

The *ethyl* ester of elæomargaric acid is a yellow liquid, b. p. 230—240°/25 mm; the *methyl* ester decomposes when warmed.

W. H. G.

Japanese Vegetable Oils. TOKUHEI KAMETAKA (*J. Coll. Sci. Tōkyō*, 1908, **25**, iv, 1—7).—*Japanese Wood Oil* (*Kiri-abura*).—The iodine number of the fresh, cold-drawn oil was found by Hübl's method to be 161·3; after storing in a stoppered bottle in the dark for eleven months, the value obtained by the same method was 150·0. The iodine number after three months, determined by Wys' method, was 156·3, and after eleven months, 153·2. The low iodine number of Japanese wood oil cannot, therefore, be ascribed to previous oxidation, as stated by some chemists (compare Ingle, *J. Soc. Chem. Ind.*, 1902, 21, 187), although the value does decrease on oxidation. Using the number 161·3, it is found by calculation that the oil consists of about 86% of elæomargarin and 14% of olein. The following constants were determined: acid number, 3·81; D_{24}^{24} 0·9307; saponification number, 196·0. An *enzyme*, capable of hydrolysing the oil and also ethyl acetate, was obtained from the seeds of *Elæococca vernicia*. Since this enzyme is present in small quantities in the oil itself, it possibly plays some part in the rapid drying of this oil.

Camellia Oil or Oil of *Thea japonica* (*Tsubaki-abura*) has D_4^{15} 0·9138 and iodine number (Hübl's method) 79·47. The principal acid in the oil is oleic acid.

Oil of *Terrya nucifera* (*Kayana-abura*) has the iodine number (Hübl's method) 137·3. It contains linolic acid or its isomerides, together with stearic acid.

Soja-bean Oil or Oil of *Glycine hispida* (*Daidzu-abura*).—The unsaturated acids in this oil are chiefly oleic acid and linolic acid or its isomerides.

Oil of *Perilla* (*Eno-abura*) appears to contain linolenic acid or its isomeride. W. H. G.

Compounds of Bismuth with Aliphatic Hydroxy-acids. Hans Telle (*Arch. Pharm.*, 1908, **246**, 484—503).—Compounds of bismuth with lactic, malic, tartaric, and citric acids have been prepared, and a new method of preparing such salts, depending on the decomposition of the soluble hydrated acid lactate with the appropriate acid, is described.

Freshly-precipitated bismuth hydroxide dissolves slowly in lactic acid slightly diluted with water, and the solution gradually deposits bunches of glancing needles of the *hydrated* salt, $BiC_6H_9O_6,7H_2O$. This is readily soluble in water, and at 105° furnishes the anhydrous salt, $BiC_6H_9O_6$, which is scarcely soluble in water, and can be obtained in rhombic tablets by digesting bismuth hydroxide with lactic acid at 100°. The anhydrous salt decomposes slightly when boiled for some time with water (compare Engelhardt, this Journ., 1848, **1**, 400, and Brunig, *Annalen*, 1857, **104**, 195).

Bismuth malate, $BiC_4H_3O_5,H_2O$, colourless needles, can be prepared either by heating bismuth hydroxide with just enough malic acid dissolved in a little water for a few minutes, or by adding a solution of malic acid to one of the hydrated lactate referred to above and boiling the mixture. It is nearly insoluble in water.

Attempts to prepare bismuthotartaric acid by Baudran's method (Abstr., 1900, i, 375) resulted in the formation of minute needles of the *hydrated* salt, $BiC_8H_9O_{12},3H_2O$, instead of the compound, $C_4H_5(BiO)O_6,H_2O$, described by Baudran (compare Rosenheim and Vogelsang, Abstr., 1906, i, 231). This can also be obtained by adding a solution of tartaric acid to one of the hydrated lactate and boiling the liquid. It is nearly insoluble in water, but dissolves in solutions of alkali hydroxides or carbonates, yielding syrups from which no crystalline product could be obtained.

Rother's bismuth citrate, $BiC_6H_5O_7$ (this Journ., 1876, ii, 173), can be prepared in a well-crystallised condition, either by dissolving bismuth hydroxide in a solution of citric acid, or from the hydrated lactate by the general method. T. A. H.

Dehydrocamphenylic Acid. GUSTAV KOMPPA and S. V. HINTIKKA (*Ber.*, 1908, **41**, 2747—2750).—By the oxidation of camphene by dilute nitric acid, Jagelki obtained an unsaturated acid, $C_{10}H_{14}O_2$, which he claimed to be identical with Wagner's dehydrocamphenylic acid (Abstr., 1899, i, 627, 629). Since the latter is saturated, the authors have re-examined Jagelki's compound, and find that it is saturated and identical with dehydrocamphenylic acid and with an acid obtained by Konowaloff (Abstr., 1907, i, 279). The *silver*, *lead*, and *calcium* salts are mentioned. The *ethyl* ester, $C_{12}H_{18}O_2$, b. p. 100—101°/10 mm., D^{20} 1·0143, n_D^{20} 1·47299, shows the molecular refraction of a saturated, tricyclic ester. The *amide*, m. p. 114·5°, and *anilide*, $C_9H_{13}\cdot CO\cdot NHPh$, m. p. 102—103°, have been prepared. C. S.

Active Pinonic and Pinic Acids. PHILLIPE BARBIER and VICTOR GRIGNARD (*Compt. rend.*, 1908, **147**, 597—600).—Previous authors, using pinene of low rotatory power, have only succeeded in obtaining racemic pinonic acid by oxidation of this terpene. When *l*-pinene (b. p. 155—157°, $[\alpha]_D$ $-37·2°$) is oxidised by potassium permanganate in the cold, a mixture of racemic pinonic acid and l-*pinonic acid* is produced. *l*-Pinonic acid, $C_{10}H_{16}O_3$, forms large crystals, m. p. 67—69°, $[\alpha]_D^{22}$ $-90·5°$ (in chloroform), and gives a mixture of two *oximes*, the γ crystallising in dextrorotatory micro-crystals, m. p. 189—191°, difficultly soluble in ether, and the β crystallising in large, lævorotatory tablets, m. p. 128°, readily soluble in ether. On oxidation by sodium hypochlorite or hypobromite, the acid gives *d*-pinic acid, having m. p. 135—136°, $[\alpha]_D^{25}$ $+7·1°$. A *d*-pinene, having D_0 0·8745, D_{14}^4 0·8635, n_D 1·46977, $[\alpha]_D$ $+39·4°$, b. p. 155—158°, on oxidation in a similar manner, gives a mixture of *d*-pinonic acid and the racemic acid. d-*Pinonic acid* has m. p. 67—68°, $[\alpha]_D^{25}$ $+89·0°$, and, when fused with an equal weight of the *l*-acid, gives immediately the racemic acid, m. p. 104°. The *d*-acid gives the β and γ oximes identical with those described by Baeyer. The conclusion is drawn that Tiemann's acid, having m. p. 98—99°, and giving an oxime, m. p. 147°, is not the true *l*-pinonic acid derived from *l*-pinene; the two acids are possibly the *cis*- and *cis-trans*-isomerides predicted by theory. E. H.

Equilibrium in the System: Potassium Oxalate, Oxalic Acid, Water. IWAN KOPPEL and M. CAHN (*Zeitsch. anorg. Chem.*, 1908, **60**, 53—112).—The equilibrium relations in the system $K_2O-CrO_3-H_2O$ have been determined over a wide range of temperature, and the results are illustrated by numerous curves and are summarised on projected space diagrams. The three potassium oxalates already known, $K_2C_2O_4,H_2O$, KHC_2O_4, and $KHC_2O_4,H_2C_2O_4,2H_2O$, exist in equilibrium with solution within certain limits of concentration at all the temperatures at which measurements have been made. Further, an acid salt of the formula $2K_2C_2O_4,H_2C_2O_4,2H_2O$ (the salt *M*), not previously known, is stable between its cryohydric point and its transition point in the neighbourhood of 84°.

In the course of the investigation, the complete isothermals have been determined at 0°, 30°, and 60° by solubility observations in the usual way, and the ice lines and boiling-point lines have also been determined. The *M*-salt is decomposed by water under all conditions, with separation of potassium hydrogen oxalate, and this salt is decomposed by water from its cryohydric point up to about 50°. Oxalic acid itself is partly decomposed when heated in aqueous solution above 100°, even in the presence of acid oxalates.

The transition temperature of the *M*-salt, represented by the equation: $2K_2C_2O_4,H_2C_2O_4,2H_2O \rightleftarrows K_2C_2O_4,H_2O + 2KHC_2O_4 + H_2O$, was determined both by solubility and dilatometer experiments, the mean value being about 84°, as mentioned above.

In preparing pure potassium hydrogen oxalate, rather more than the theoretical amount of alkali should be employed, otherwise the salt which separates from solution is contaminated with tetroxalate. Observations have been made which support Wyrouboff's statement, that the acid oxalate exists in two forms: an anhydrous modification in monoclinic crystals, stable above 15°, and a monohydrate in orthorhombic crystals, which separates from solution below 15°. G. S.

Decomposition of Lead Oxalate by Saline Solutions. H. CANTONI and L. MAURI (*Bull. Soc. chim.*, 1908, [iv], 3, 929—935). —An extension of the investigation previously described (Abstr., 1906, i, 557) on the action of alkali sulphates on oxalates of the alkaline earths to the case of lead oxalate reacting with solutions of alkali chlorides or sulphates. Tables of the numerical results obtained are given in detail in the original. These show that alkali sulphates in solution decompose lead oxalate, and that the extent of this decomposition increases (1) with rise of temperature, (2) time of action, and (3) concentration of the solution. Of the three sulphates tried, namely, potassium, sodium, and ammonium, the first is the most active and the third least, but the potassium salt is relatively much more active than either of the other two. The alkali chlorides attack the oxalate far less readily than do the sulphates, and there is little to choose between the three chlorides tried in this respect. In the cold, neither alkali sulphates nor chlorides exert any considerable action on lead oxalate. T. A. H.

Complex Ferrimalonates. MOTOOKI MATSUI (*J. Coll. Sci. Tōkyō*, 1908, **25**, ii, 1—5).—Complex ferrimalonates having the composition $(CO_2M\cdot CH_2\cdot CO_2)_3Fe$, where M represents either sodium, potassium, or ammonium, have been prepared by adding ferric chloride to an aqueous solution of the malonate so long as the mixed solution did not give a red coloration with potassium thiocyanate. These salts are decomposed by acids and alkalis; in aqueous solution, they dissociate into the complex ion, $[Fe(CO_2\cdot CH_2\cdot CO_2\cdot)_3]'''$, and the ion of the alkali metal. The aqueous solution is unstable, the green colour soon changing into brown; it is probable that the decomposition is due to hydrolysis, since the addition of sodium malonate renders the solution stable. The *acid* corresponding with these salts has not yet been isolated, but it is obtained in aqueous solution by dissolving moist ferric hydroxide in a warm solution of malonic acid.

Sodium ferrimalonate, $Fe(CO_2{\cdot}CH_2{\cdot}CO_2{\cdot}Na)_3$, forms green, sandy crystals and decomposes at about 200°. *Potassium ferrimalonate*, $Fe(CO_2{\cdot}CH_2{\cdot}CO_2K)_3,4H_2O$, crystallises in green prisms. *Ammonium ferrimalonate*, $Fe(CO_2{\cdot}CH_2{\cdot}CO_2{\cdot}NH_4)_3,4H_2O$, forms green, prismatic crystals. The *barium* and *calcium* salts were prepared, but not analysed.

Ferrous iron also forms complex malonates, which are precipitated as yellow crystals by adding alcohol to an aqueous solution of a malonate and ferrous sulphate. They are very unstable, and immediately change in the air to the corresponding ferric compounds.

W. H. G.

Formation of Compounds in Solutions of Tartaric Acid and Sodium Molybdate. HERMANN GROSSMANN (*Zeitsch. anorg. Chem.*, 1908, **60**, 50—52).—Remarks on a recent paper by Quinet (this vol., i, 713). Priority is claimed for certain results described in Quinet's paper (Rosenheim and Itzig, Abstr., 1900, i, 135, 272; Grossmann and Pötter, 1906, i, 799). Further, it is pointed out that the mixture of tartaric acid and sodium molybdate of maximum rotatory power contains the components in the ratio $1C_4H_6O_6 : 1Na_2MoO_4$, and not 1 : 2 as given by Quinet, and that the other characteristic point corresponds with the composition $C_4H_6O_6 : \frac{1}{2}Na_2MoO_4$. G. S.

Some Citrates. E. I. VAN ITALLIE (*Pharm. Weekblad*, 1908, **45**, 1201—1210).—The action of ammonia on aqueous solutions of citric acid at 30° only yields known hydrates; that of calcium hydroxide at the same temperature produces the hydrates $(C_6H_7O_7)_2Ca,3H_2O$ and $C_6H_6O_7Ca,4H_2O$. A. J. W.

Action of Calcium Carbide on Some Ketones. F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1908, [iv], **3**, 829—833).—Acetone prepared from its sodium hydrogen sulphite compound reacts energetically with powdered calcium carbide, evolving acetylene and forming mesityl oxide and more complex substances boiling between 170° and 350°. Whatever the conditions, the proportion of mesityl oxide only varies from 8% to 12%; the yield of the higher boiling products, on the other hand, depends on the length of time the acetone is in contact with the carbide. Commercial acetone, the vapour of which acts on fragments of calcium carbide, has no action on the latter when powdered. Pure butanone also acts on calcium carbide, although more slowly, giving, besides higher boiling products, an agreeably smelling *ketone*, $C_8H_{14}O$, b. p. 164—166°/760 mm. and 66—68°/20 mm., D^{25} 0·853. This is probably either ζ-methyl-Δ^{δ}-heptene-γ-one,

$$CH_2Me{\cdot}CO{\cdot}CH{:}CMe{\cdot}CH_2Me,$$

or γδ-dimethyl-Δ^{γ}-hexene-β-one, $CH_2Me{\cdot}CMe{:}CMe{\cdot}COMe$, or a mixture of the two. If commercial butanone, dried over potassium carbonate and rectified, is used, the new ketone apparently contains a liquid richer in oxygen.

Boiling δ-pentanone and acetophenone have no action on calcium carbide. The vapour of the latter ketone at ordinary, but not at reduced, pressure acts on the carbide, giving a gummy mass.

The author finds that certain esters retard or altogether prevent the action of acetone, and draws the conclusion that the inactivity of commercial acetone is due to its containing an impurity of this nature.

E. H.

Reduction of *αβ*-Unsaturated Ketones. ALADAR SKITA, A. ARDAN, and M. KRAUSS (*Ber.*, 1908, 41, 2938—2946).—The paper deals with the comparative study of the reduction of aliphatic and alicyclic *αβ*-unsaturated ketones by Sabatier and Senderens' method.

Mesityl oxide, reduced at 185° for seven hours, yields methyl *iso*butyl ketone in 60% yield and a small quantity of methyl*iso*butylcarbinol; reduced for eight hours at 210° in a more rapid current of hydrogen (220 c.c. per minute), mesityl oxide yields *β*-methylpentane (compare Darzens, Abstr., 1905, i, 66, 172). Phorone, reduced at 225° for five hours (velocity of hydrogen = 100 c.c. per minute), gives a 65% yield of valerone, whilst at 235° and with a velocity of 280 c.c. of hydrogen per minute, the products are valerone and an unidentified, unsaturated hydrocarbon, di*iso*butylcarbinol, and *βζ*-dimethylheptane.

1 : 3-Dimethyl-Δ^3-*cyclo*hexen-5-one, reduced for six hours at 235° (velocity of hydrogen = 100 c.c. per minute), yields 1 : 3-dimethyl*cyclo*hexane, b. p. 119—120°, D^{20} 0·7822. Ethyl 1-methyl-Δ^6-*cyclo*hexen-5-one-2-carboxylate (Hagemann, Abstr., 1893, i, 393), reduced for four hours at 280—285° with an equally rapid current of hydrogen, yields ethyl 1-methyl-$\Delta^{4\,(\text{or }5)}$-*cyclo*hexene-2-carboxylate, of which the acid has b. p. 114—130°/9 mm., and forms a crystalline *dibromide*, $C_8H_{12}O_2Br_2$.

C. S.

Density of Sucrose. G. FOUQUET (*Bull. Assoc. Chim. Sucr. Dist.*, 1908, 26, 176—177).—The author finds that different methods of crystallising sucrose produce crystals of varying density; one specimen of crystals examined had D 1·550 to 1·575, whilst another had D 1·580 to 1·610. The actual cause which produces the variation in the density has not yet been ascertained.

W. P. S.

Aqueous Solutions and their Densities: Sucrose Solutions. G. FOUQUET (*Bull. Assoc. Chim. Sucr. Dist.*, 1908, 26, 160—176).—The curve of contractions occurring when sucrose is dissolved in water, calculated on the value 1·590 for D^{15}_{15} of sucrose, exhibits a maximum for 40% by weight of sucrose, whilst for a saturated solution (66—67% of sucrose) the contraction is zero. The above value for the density of sucrose is calculated from the value D^{15}_{4} 1·5881. For concentrations up to 15%, the contraction is sensibly proportional to the concentration, whilst for concentrations (p) up to 40%, the contraction is represented by the formula: $\delta = 0·000225p(80 - p)$. When p increases from 5% to 75%, the density of the sugar in solution diminishes continuously, and the same is probably the case for increase of p from 0% to 5%, although here the increase is only slight. For concentrations up to 5%, the values of D^{15}_{4} for sucrose solutions are represented by the expression: $162{\cdot}91956/(163{\cdot}05 - 0{\cdot}6313\,p)$. These considerations are extended to impure sucrose solutions. T. H. P.

Inversion of Sucrose. YUKICHI OSAKA (*J. Coll. Sci. Tōkyō*, 1908, 25, i, 1—8).—It is shown that, whereas in moderately dilute solutions the hydrolysis of sucrose by an acid may be regarded as practically complete, in strong solutions (80 grams of sugar in 100 c.c. of solution) the hydrolysis is incomplete. It is therefore probable that the inversion of sucrose by an acid is a reversible reaction. This view is supported by the result of the following experiment. A solution of about 20 grams of sucrose in 50 c.c. of solution was hydrolysed completely by hydrochloric acid; 5·7507 grams of this solution, treated with sodium acetate and diluted to 25 c.c., gave a rotation of −3·83°. The same weight of the inverted solution (5·7507 grams) was then concentrated to about one-half by passing dry air over the surface of the solution; it was then treated with sodium acetate and made up to 25 c.c. as before; this solution had a rotation of −3·30°. The reversion product could not be maltose or *iso*maltose, since the author finds that no reversion takes place in concentrated solutions of dextrose under the influence of an acid at 25° during a period of two months. W. H. G.

Inversion of Sucrose by Invertase. II. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1908, 30, 1564—1583).—A continuation of the work previously recorded (this vol., i, 605). The results completely confirm O'Sullivan and Tompson's conclusions (Trans., 1890, 51, 834).

The velocities of the mutarotation of dextrose and lævulose at 30° in water and in aqueous solutions of hydrochloric acid and invertase have been determined. The velocities are not affected by invertase, but are greatly accelerated by acids. This difference between the action of invertase and acids on the products of the inversion of sucrose causes the action of invertase to appear irregular, owing to the influence of the mutarotation of the invert-sugar on the polarimetric reading. On correcting for this, the inversion of sucrose by invertase proves to be a catalytic reaction of the first order.

The acceleration of the mutarotation of dextrose at 30° by hydrochloric acid is such that the rate is a linear function of the hydrogen-ion concentration. In the case of lævulose, a minimum rate occurs in dilute acid solutions similar to the less pronounced minimum which has been found in the case of dextrose at 25° (Abstr., 1907, ii, 942).

The action of invertase is greatly accelerated by minute traces of acid, but the addition of further small quantities of acid does not increase the effect. The inversion of sucrose, in both dilute and concentrated solutions, by invertase is proportional to the concentration of the invertase.

A method is given for calculating the amounts of fresh dextrose and lævulose that are present at any instant in the solution undergoing inversion. This method is also applicable to the determination of the forms in which the various hexoses are liberated from glucosides and di- and tri-saccharides by the action of enzymes. It is shown that the dextrose formed from sucrose by the action of invertase has $[\alpha]_D$ 100—125°, and is therefore in the form of α-dextrose ($[\alpha]_D = 106°$). E. G.

Action of Cold Aqueous Sodium Hydroxide on Cellulose. II. WALTHER VIEWEG (*Ber.*, 1908, **41**, 3269—3275. Compare Abstr., 1907, i, 893).—From 11% to 24% sodium hydroxide solutions, cellulose takes up an amount of the alkali sufficient to form the compound $C_{12}H_{19}O_{10}Na$, and, if the results are plotted, the curve obtained is discontinuous, the point of discontinuity corresponding with the formation of this compound. The curve up to this point is abnormal, but afterwards it is a horizontal straight line pointing to a chemical reaction. It is also shown that the higher the degree of mercerisation the greater the capacity for absorption of sodium hydroxide, and more is taken up at lower than at higher temperatures. Contrary to the statement of Miller (this vol., i, 78), the addition of sodium chloride to the sodium hydroxide increases the absorption, and the conclusion is drawn that the reaction is physical as well as chemical. W. R.

Walden's Inversion. III. EMIL FISCHER and HELMUTH SCHEIBLER (*Ber.*, 1908, **41**, 2891—2902. Compare Abstr., 1907, i, 192; this vol., i, 324).—The optical properties of valine (α-amino*iso*valeric acid) are not altered by the double transformation into bromo-fatty acid and back to amino-compound. There are some reasons for thinking that this is due rather to a double Walden inversion than to its absence.

d-Valine forms *l*-α-bromo*iso*valeric acid, which, when coupled with valine and treated with ammonia, yields l-*valyl*-d-*valine*. This dipeptide yields racemic valine on hydrolysis, and forms also *trans*-valine anhydride. *l*-Valine, when treated with nitrosyl bromide, forms *d*-α-bromo*iso*valeric acid, from which *d*-valylglycine is obtained on treatment with ammonia and *d*-valine on subsequent hydrolysis. Thus *d*-bromo*iso*valeric acid yields *l*-valine, and *d*-bromo*iso*valerylglycine yields *d*-valine. The ester of *d*-bromo*iso*valeric acid likewise appears to yield *d*-valine.

Both silver oxide and potassium hydroxide, acting on *d*-bromo*iso*valeric acid, give rise to the same hydroxy*iso*valeric acid, which is dextrorotatory in alkaline solution. *d*-Bromo*iso*valerylglycine, treated with silver oxide in a similar manner, yields a highly optically active hydroxy-compound, which, on hydrolysis, gives rise to the same dextrorotatory hydroxy*iso*valeric acid. This acid is also formed from *l*-valine by the action of nitrous acid, which in this case produces inversion, an observation quite contrary to what has been observed for alanine or aspartic acid.

The α-*hydroxy*iso*valeric acid*, prepared by means of silver oxide, has in normal sodium hydroxide, $[\alpha]_D^{20}$ +11·8°; prepared using potassium hydroxide, it has $[\alpha]_D^{20}$ +12·0°; nitrous acid yields the same compound, $[\alpha]_D^{20}$ +12·2°.

d-*α-Bromo*iso*valerylchloride*, $C_3H_7\cdot CHBr\cdot COCl$, has b. p. 54—55°/13 mm. (corr.). d-*α-Bromo*iso*valerylglycine*,

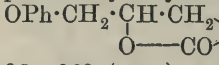
$$C_3H_7\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

forms large, well-formed, radiating prisms, m. p. 119—120° (corr.) to a colourless liquid after sintering at 115° (corr.). It has $[\alpha]_D^{20}$ +47·5°. The *α-hydroxy*iso*valeric acid* obtained from this by means of silver oxide has $[\alpha]_D^{20}$ +11·8°.

The *zinc* salt of active *α-hydroxy*iso*valerylglycine* crystallises in silvery, four-cornered prisms, $[\alpha]_D^{20}$ +48·7° in water and +36·1° in *N*-hydrochloric acid. E. F. A.

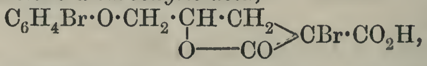
Preparation of α-Amino-γδ-dihydroxy-*n*-valeric Acid. Emil Fischer and Adolf Krämer (*Ber.*, 1908, 41, 2728—2739).—In view of the general occurrence of serine in the scission products of proteins, and the formation of hydroxyproline in the hydrolysis of gelatin, it is probable that other aliphatic aminohydroxy-acids are formed by the decomposition of proteins. Among these are to be expected derivatives of *n*-valeric and *n*-hexoic acids, owing to their relation to ornithine and lysine. α-Amino-δ-hydroxy-*n*-valeric acid has already been synthesised by Sörensen (Abstr., 1905, i, 749), and converted into *r*-proline by hydrochloric acid. The authors have now made experiments on the synthesis of an aminodihydroxy-acid, which should stand in a similar relation to hydroxyproline, and to this end have employed the method used by Fischer and Blumenthal (Abstr., 1907, i, 191) for the synthesis of α-amino-γ-hydroxybutyric acid.

γ-Chloro-β-hydroxy-α-phenoxypropane, $OPh\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$, prepared by heating epichlorohydrin with phenol under pressure, is a colourless, viscid oil, b. p. 152—153°/12 mm., with a rancid odour and a bitter taste; when treated with ethyl sodiomalonate and the product hydrolysed, it yields *δ-phenoxy-γ-valerolactone-α-carboxylic acid*,



$$\begin{array}{l} OPh\cdot CH_2\cdot \overset{}{C}H\cdot CH_2 \\ \qquad\quad O\text{———}CO \end{array}\!\!>CH\cdot CO_2H,$$

in slender needles, sintering at 93—96° (corr.) and evolving gas at a higher temperature. A chloroform solution of this gives with bromine, *α-bromo-δ-bromophenoxy-γ-valerolactone-α-carboxylic acid*,



$$\begin{array}{l} C_6H_4Br\cdot O\cdot CH_2\cdot CH\cdot CH_2 \\ \qquad\qquad\qquad O\text{———}CO \end{array}\!\!>CBr\cdot CO_2H,$$

forming slender needles, m. p. 157° (corr.), losing carbon dioxide when heated, with the production of *α-bromo-δ-bromophenoxy-γ-valerolactone*, which crystallises in slender, microscopic needles or rods and sometimes prisms, m. p. 128° (corr.). By the action of ammonia, this is converted into *α-amino-δ-bromophenoxy-γ-valerolactone*, which forms microscopic, slender, colourless leaflets, m. p. 230° (corr., decomp.); the *hydrochloride* has m. p. 229° (corr., decomp.), and the *hydrobromide* has m. p. 235° (corr., decomp.). The aminolactone dissolves in alkalis, forming salts of α-amino-γ-hydroxy-δ-bromophenoxyvaleric acid, of which the *silver* salt was analysed. When the aminolactone is heated under pressure with concentrated hydrobromic acid and the product hydrolysed (to remove combined bromine), a mixture of amino-acids is obtained, which can be separated by means of the copper salts. The sparingly soluble product is the copper salt of (*a*)γ-hydroxyproline (Leuchs, Abstr., 1905, i, 545), and the readily soluble one is probably *copper* α-*amino*-γδ-*dihydroxy*-n-*valerate*; it forms small, dark blue leaflets. The *acid*,

$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$,

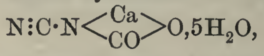
prepared from the copper salt by treatment with hydrogen sulphide, forms bushy needles, m. p. 160—165°. J. C. C.

Action of Certain Oxidising Agents on Thiocyanic Acid. C. Bongiovanni (*Gazzetta*, 1908, **38**, ii, 299—301).—The author has shown previously (Abstr., 1907, i, 833; this vol., i, 770) that the product of the reaction between a ferric salt and a thiocyanate is a salt of the composition $Fe(CNS)_3$, and not a peroxygenated salt, as Tarugi (Abstr., 1905, i, 176) supposes. Further experimental evidence in support of this view is now adduced.

When freshly-prepared nickel or cobalt hydroxide is treated for some days with a 3% thiocyanic acid solution, it is converted into the nickelous or cobaltous salt of the acid without any formation of red hyper-acid occurring. Further, the addition of acid produces no red coloration, as it should do if the reaction resulted in the formation of a colourless salt of the type $Na_3C_3N_3S_3O_3$. It is found that the thiocyanic acid is not decomposed, owing to the strong oxidising action of the nickel or cobalt hydroxide, and that the salt formed has no oxidising properties. Molybdenum thiocyanate has a red colour, but is only formed in presence of a reducing agent, which cannot, of course, determine the formation of a hyper-acid. T. H. P.

Supposed Ammoniacal Fermentation of Cyanamide. Celso Ulpiani (*Gazzetta*, 1908, **38**, ii, 358—417).—The experiments of Löhnis (Abstr., 1905, ii, 412) and of Löhnis and Sabaschnikoff (this vol., ii, 220) on the formation of ammonia from calcium cyanamide by the action of bacteria led to erroneous conclusions, because (1) "Kalkstickstoff" gradually undergoes change, and only when freshly prepared does it contain one single nitrogenous compound, calcium cyanamide; (2) after sterilisation by heating, solutions of calcium cyanamide contain no trace of the latter, and (3) many amidic substances, besides ammonium salts, yield ammonia when their solutions are distilled with magnesia at the ordinary pressure. From the fact that "Kalkstickstoff" solutions which have not been sterilised by heating do not undergo bacterial decomposition, Löhnis assumes that the action of heat results in the conversion of the asymmetric form of cyanamide, $N{:}C\cdot NH_2$, into the symmetrical form, $NH{:}C{:}NH$, which alone is attackable by bacteria; this assumption the author shows to be superfluous.

The preparation of pure cyanamide from calcium cyanamide, which is complicated by the tendency of the cyanamide to polymerise into dicyanodiamide, may be affected as follows. One part of "Kalkstickstoff" is thoroughly mixed with four parts of cold water, and through the filtered solution, cooled with ice, a current of carbon dioxide is passed. The calcium cyanamidocarboxylate,



$$N{:}C{\cdot}N{<}{}^{Ca}_{CO}{>}O,5H_2O,$$

thus precipitated may be converted into (1) dicyanodiamide by drying at the ordinary temperature or in an oven, $2(C_2O_2N_2Ca,5H_2O) = 8H_2O + 2CaCO_3 + (CN_2H_2)_2$, or (2) cyanamide by triturating with water and subjecting the mass to the prolonged action of carbon dioxide; $C_2O_2N_2Ca + H_2O = CaCO_3 + CH_2N_2$.

The decomposition of pure cyanamide takes place far more slowly than that of cyanamide accompanied by the secondary products also present in "Kalkstickstoff," and proceeds as well in the presence as in the absence of chloroform, all possibility of bacterial action being thus excluded. The factors which determine the decomposition of cyanamide are calcium, soil, and the secondary products of "Kalkstickstoff," which are capable, in presence of bacteria and of a suitable nutritive medium, of yielding ammonia. These secondary products are found to be: (1) Carbamide, formed by hydrolysis of the cyanamide. (2) Dicyanodiamide, formed by polymerisation. (3) Aminodicyanic acid, $CN{\cdot}NH{\cdot}CO{\cdot}NH_2$, separated in the form of its copper salt, $Cu(C_2H_2ON_3)_2,4H_2O$, which, when treated with hydrogen sulphide, gives, not the free acid, but thiobiuret, $CN{\cdot}NH{\cdot}CO{\cdot}NH_2 + H_2S = NH_2{\cdot}CS{\cdot}NH{\cdot}CO{\cdot}NH_2$. Aminodicyanic acid is formed by the hydrolysis of the dicyanodiamide in presence of lime:

$$CN{\cdot}NH{\cdot}C(NH_2){:}NH + H_2O = CN{\cdot}NH{\cdot}CO{\cdot}NH_2;$$

if the hydrolysis is effected by means of acid, dicyanodiamidine is formed: $CN{\cdot}NH{\cdot}C(NH_2){:}NH + H_2O = NH_2{\cdot}CO{\cdot}NH{\cdot}C(NH_2){:}NH$. (4) Ammeline, formed by the hydrolysis of melamine, $C_3H_6N_6 + H_2O = C_3H_5ON_5 + NH_3$, itself produced by polymerisation of the cyanamide. When free from acids and bases, a solution of cyanamide remains unchanged at the ordinary temperature.

A list of papers previously published on this subject is given, and the results given therein discussed. T. H. P.

The Biochemical Conversion of Glutamic into *n*-Butyric Acid. WALTHER BRASCH and CARL NEUBERG (*Biochem. Zeitsch.*, 1908, **13**, 299—304).—*n*-Butyric acid was shown by Neuberg and Rosenberg to account for about one-third of the volatile fatty acids obtained from the putrefaction of caseinogen. As aminobutyric acid has not been definitely proved to be a product of hydrolysis, glutamic acid was assumed to be the source of the volatile acid:

$$CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3.$$

By actual putrefaction experiments with glutamic acid, butyric acid was obtained to the amount of about 58·6% of the theoretically possible quantity. The other acids formed were formic and succinic acids. Glutaric acid was not obtained, nor did the latter acid yield *n*-butyric acid when treated with putrefying organisms. S. B. S.

α-Camphoramic Acids. MLLE. G. FREYLON (*Ann. Chim. Phys.*, 1908, [viii], **15**, 278—288).—The author has shown (this vol., i, 827) that α-aminoethylbenzene condenses with camphoric anhydride to form two ethylbenzene-α-camphoramic acids, which are enantiomorphously related to one another; in the present paper, the substituted α-camphoramic acids obtained similarly from diethylamine, β-aminobutane, and γ-amino-octane are described, but, although each of the last two bases contains an asymmetric carbon atom, they do not furnish stereoisomeric α-camphoramic acids.

Diethyl-α-camphoramic acid, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NEt_2$, crystallises in needles, m. p. 169—170°, and has $[\alpha]_D^{20}$ +19·29° in alcoholic solution.

β-Butyl-α-camphoramic acid, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NH \cdot C_4H_9$, has m. p. 206—208°, and $[\alpha]_D^{20}$ +28·80° in alcoholic solution.

δ-Amino-octane, $C_3H_7 \cdot CH(NH_2) \cdot C_4H_9$, prepared by reducing the *oxime*, $C_3H_7 \cdot C(NOH) \cdot C_4H_9$, b. p. 116—117°/20 mm., by means of sodium and alcohol, has b. p. 64—65°/18 mm., and forms a *hydrochloride*, m. p. 194—195°, and a *carbonate*; the corresponding *carbamide*,

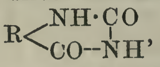
$$NH_2 \cdot CO \cdot NH \cdot C_8H_{17},$$

has m. p. 166—168°. When heated for six hours at 120° with camphoric anhydride, it yields *δ-octyl-α-camphoramic acid*,

$$CO_2H \cdot C_8H_{14} \cdot CO \cdot NH \cdot C_8H_{17},$$

which has m. p. 177—178°, and $[\alpha]_D^{20}$ +24·45°. M. A. W.

Carbamido-acids. II. and III. FRITZ LIPPICH (*Ber.*, 1908, 41, 2953—2974, 2974—2983. Compare Abstr., 1906, i, 813).—II.—The author finds that the Baumann and Hoppe-Seyler reaction for the preparation of hydantoic acid (this Journ., 1874, 466) is a general reaction of amino-acids, and presents a simple method for the preparation of carbamido-acids. The present communication deals with the α-amino-acids of the glycine series, aspartic and glutamic acids, taurine, and tyrosine. The reaction takes place by heating the amino-acid for six to ten hours with two to three times its weight of carbamide and 200—500 c.c. of baryta water, and is represented by the equation: $NH_2 \cdot R \cdot CO_2H + CO(NH_2)_2 = CO_2H \cdot R \cdot NH \cdot CO \cdot NH_2 + NH_3$.

The carbamido-acids so obtained give flocculent precipitates with mercuric nitrate in the absence of chlorides or free acid, crystalline compounds with alcoholic mercuric chloride or silver nitrate, do not respond to the biuret test, yield hydantoins,  $R<\begin{matrix} NH \cdot CO \\ CO-NH \end{matrix}$, by treatment with cold concentrated or with warm dilute mineral acids, and are hydrolysed by hot alkalis or hot concentrated hydrochloric acid, regenerating the amino-acid.

Hydantoic acid (carbamidoacetic acid) has m. p. 163° in a sealed capillary tube (compare Weidel and Roitner, Abstr., 1906, i, 470); the *barium*, *copper*, *lead*, *mercury*, and *silver* salts are described. α-Carbamidopropionic acid and α-carbamido*iso*butyric acid are known in the literature as lacturamic acid (Urech, this Journ., 1873, 380) and acetonyluramic acid respectively. *α-Carbamido*isovaleric *acid*,

$$CHMe_2 \cdot CH(NH \cdot CO \cdot NH_2) \cdot CO_2H,$$

m. p. 176°, separates from water in tufts of long needles; the *barium*, *mercury*, and *silver* salts are described. α-Carbamido*iso*hexoic acid (*iso*butylhydantoic acid: compare Pinner and Spilker, Abstr., 1889, 704) yields crystalline *barium*, *lead*, *copper*, *mercury*, and *silver* salts. The acids prepared from leucine, obtained from different sources, show slight differences in solubility, m. p., and per cent. of nitrogen; these are explained by specific differences in the original leucines.

α-Carbamidosuccinic acid, $CO_2H\cdot CH_2\cdot CH(NH\cdot CO\cdot NH_2)\cdot CO_2H$, m. p. 162°, prepared from aspartic acid, separates from dilute alcohol in rhombic plates or prisms; the *copper*, *lead*, *mercury*, *silver*, and *silver hydrogen* salts are mentioned. *α-Carbamidoglutaric acid*,

$$CO_2H\cdot CH_2\cdot CH_2\cdot CH(NH\cdot CO\cdot NH_2)\cdot CO_2H,$$

m. p. 150°, crystallises in needles. Taurocarbamic acid, obtained by Salkowsky (this Journ., 1874, 148), and later by Gabriel, is prepared very readily by the author's method. α-Carbamido-β-*p*-hydroxyphenylpropionic acid, $OH\cdot C_6H_4\cdot CH_2\cdot CH(NH\cdot CO\cdot NH_2)\cdot CO_2H$, m. p. 218° (decomp.), is identical with Jaffe's tyrosinehydantoic acid (*Zeitsch. physiol. Chem.*, 1882, **7**, 306). The anhydride, tyrosinehydantoin, has m. p. 242—245° (decomp.).

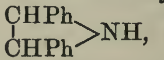
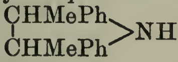
III.—The Baumann and Hoppe-Seyler reaction has been successfully applied to anthranilic, metanilic, sulphanilic, and β-aminobutyric acids and to β-phenylalanine.

Other general methods for the preparation of carbamido-acids are: (*a*) an amino-acid and a urethane are boiled with aqueous barium hydroxide. Applied to leucine and *iso*amyl carbamate, a 40% yield of α-carbamido*iso*hexoic acid is obtained. (*b*) An amino-acid is boiled with an excess of a concentrated aqueous solution of carbamide. The reaction really occurs between the amino-acid and ammonium cyanate; the continuous removal of the latter destroys the equilibrium of the system carbamide $\rightleftarrows$ ammonium cyanate (compare Walker and Hambly, Trans., 1895, **67**, 746). The method is advantageously used in the case of optically active amino-acids, since the reaction occurs in the absence of acid or alkali. Applied to leucine from different sources, the method yields α-carbamido-α-*iso*hexoic acids, which again show slight differences in physical properties. Similarly, glycine gives ammonium hydantoate, $C_3H_5O_3N_2(NH_4),H_2O$; aspartic acid is converted into α-carbamidosuccinic acid, which is isolated as the *hydantoin*, $C_5H_6O_4N_2$, m. p. 208° (decomp.), whilst tyrosine very readily yields the ammonium salt of the corresponding carbamido-acid. Leucine and potassium cyanate in boiling aqueous solution give an 83% yield of the carbamido-acid. (*c*) Prolonged boiling of an aqueous solution of an amino-acid and guanidine carbonate. The method has been used successfully with leucine and with tyrosine. C. S.

Synthesis of α-ω-Aminoguanidinehexoic Acid. Fritz Heckel (*Monatsh.*, 1908, **29**, 779—785).—Lysine, which was the starting point of this synthesis, was prepared from the sparingly soluble phosphotungstates obtained by fractional precipitation with phosphotungstic acid of the acid-hydrolytic products of casein; the precipitate is dissolved in aqueous ammonia, treated with barium hydroxide, and the mixture of amino-acids separated by means of the picrates, that of arginine being more soluble than lysine picrate. The latter is then converted into the dihydrochloride. This is treated in aqueous solution with silver cyanamide; after separating unchanged lysine by means of silver nitrate, an uncrystallisable syrup of the *base* was obtained. The *copper nitrate* compound,

$$(C_7H_{16}O_2N_4)_2,Cu(NO_3)_2,2H_2O,$$

forms dark blue, crystalline platelets; the anhydrous salt has m. p. 210° (decomp.). The compound of the nitrate with silver nitrate, $C_7H_{16}O_2N_4,AgNO_3,HNO_3$, forms white needles, blackening at 60°, m. p. 125° (decomp.). The nitrate has $[\alpha]_D + 5{\cdot}37°$. J. C. C.

Reduction of Nitriles in Neutral Solutions. HEINRICH BRUNNER and A. RAPIN (*Chem. Zentr.*, 1908, ii, 676—677; from *Schweiz. Woch. Chem. Pharm.*, 1908, **46**, 455—457).—Reduction is effected most rapidly by using a magnesium-copper couple, the reaction only taking place with Devarda's alloy when warmed. In both cases the action is identical, but the yield is better when Devarda's alloy is used. Hydrogen cyanide gives, on reduction, formaldehyde and ammonia. Acetonitrile gives acetaldehyde, ethylamine, and ammonia. Propionitrile gives propaldehyde, ethylamine, methylethylamine, methylpropylamine, and ammonia. *n*-Butyronitrile yields butaldehyde, butylamine, dibutylamine, and ammonia. Benzonitrile gives benzaldehyde, benzylamine, dibenzylamine, *diphenylethylenimide*,  $\begin{matrix}CHPh\\|\\CHPh\end{matrix}\!>\!NH$, and ammonia. *o*-Toluonitrile gives *o*-xylylamine. *m*-Toluonitrile gives *m*-tolualdehyde, *m*-xylylamine, *m*-dixylylamine, and ammonia. *p*-Toluonitrile yields *p*-tolualdehyde, *p*-xylylamine, *p*-dixylylamine, *ditolylethylenimide*,  $\begin{matrix}CHMePh\\|\\CHMePh\end{matrix}\!>\!NH$, and ammonia. *o*-Cyanodiphenylmethane gives *o*-aminodiphenylmethane, $CH_2Ph{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2$. *m*- and *p*-Cyanodiphenylmethane give *m*- and *p*-aminodiphenylmethanes. *Diphenylethylenimide* forms a very sparingly soluble nitrite and nitrate; the hydrochloride is more soluble, and the sulphate very soluble in water.

Salts of *ditolylethylenimide* are more readily soluble.

Catalytic Action of Ethylamine.—It is mentioned that a few drops of this substance hastens the reaction between methyl iodide or ethyl iodide and sodium; the behaviour of acetonitrile in this respect (Abstr., 1901, i, 457) is probably due to ethylamine formed by its reduction. J. V. E.

Preparation of Mercuric Cyanide. ERWIN RUPP and S. GOY (*Chem. Zentr.*, 1908, ii, 773; from *Apoth. Zeit.*, 1908, **23**, 373—374).—When mercuric chloride and potassium cyanide are brought together in water, considerable heat is developed, and the compound

$$HgCy_2,KCl,H_2O$$

crystallises on cooling. The same product is obtained from mercuric cyanide and potassium chloride. In a similar manner, the analogous compound is prepared from mercuric cyanide and potassium bromide, but with mercuric cyanide and potassium iodide, as also from mercuric iodide and potassium cyanide, the triple salt,

$$HgI_2,HgCy_2,2KCy,$$

crystallises in large needles. The preparation of pure mercuric cyanide is effected by treating sodium cyanide with mercuric sulphate in the presence of water; the solution becomes very warm, and, on cooling, practically pure mercuric cyanide separates out. J. V. E.

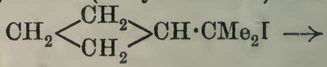
Saturated Compounds of the *cyclo*Hexane Group. NICOLAI D. ZELINSKY (*Ber.*, 1908, **41**, 2676—2680).—cyclo*Hexylpropionic acid* is prepared by the following series of reactions. ω-Iodomethyl*cyclo*hexane (b. p. 82—83°/10 mm., D_4^{19} 1·5310) is condensed with ethyl sodiomalonate, and the *ethyl hexahydrobenzylmalonate* formed, b. p. 145—155°/12 mm., hydrolysed to *hexahydrobenzylmalonic acid*, m. p. 106·5°. On heating the latter at 170°, it loses carbon dioxide and yields cyclo*hexylpropionic acid*, b. p. 143·5°/11 mm., D_4^{20} 0·9966, n_D^{20} 1·4364; the *amide* forms thin, soft needles, m. p. 120° (corr.).

[With D. SCHWEDOFF.]—cyclo*Hexylglycollic acid*, prepared by treating the hydrogen sulphite compound of hexahydrobenzaldehyde with potassium cyanide and hydrolysis of the resulting nitrile, crystallises from acetone in silvery scales, m. p. 166°. ω-*Nitromethyl*cyclo*hexane*, prepared by the interaction of ω-iodomethyl*cyclo*hexane and silver nitrite, has b. p. 98°/10 mm., D_4^{20} 1·0473, n_D^{20} 1·4688. From its salts, acids precipitate the labile *aci*-form as a heavy, golden-yellow oil, which slowly resumes the stable form.

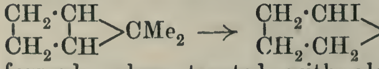
2-*Chloro*-1-*methyl*cyclo*hexane*, prepared by the action of fuming hydrochloric acid on 1-methyl*cyclo*hexan-2-ol, is stereoisomeric with the compound obtained by the action of phosphorus pentachloride. It has b. p. 91—92°/100 mm., D_4^{20} 0·9699, n_D^{20} 1·4575, and with magnesium and carbon dioxide furnishes *cis*-1-methyl*cyclo*hexane-2-carboxylic acid, b. p. 122—123°/10 mm., of which the *amide* forms slender needles, m. p. 151—153°. [The author has overlooked the fact that this *cis*-acid has already been described by Freer and Perkin, jun. (Trans., 1888, **53**, 208), and Goodwin and Perkin, jun. (Trans., 1895, **67**, 125).]
J. C. C.

Isomeric Changes in the Transformations of *cyclo*Butyldimethylcarbinol. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 994—1015. Compare this vol., i, 530).—The transformations of *cyclo*butyldimethylcarbinol as yet studied are all abnormal changes, and the preparation from this carbinol of a hydrocarbon of the tetramethylene series has not yet been effected, all the methods employed for this purpose yielding products of isomeric change. This isomeric change of the carbon skeleton of *cyclo*butyldimethylcarbinol either leads exclusively to the formation of *cyclo*pentane derivatives or is complicated by the formation of *cyclo*hexane derivatives, according to the conditions under which it takes place.

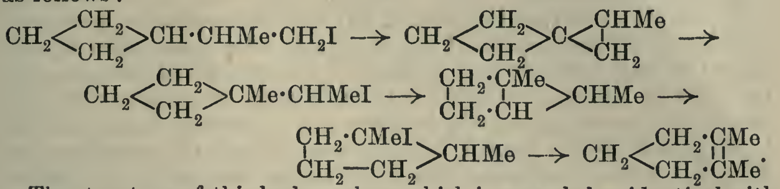
The formation of derivatives of 1 : 1-dimethyl*cyclo*pentane from *cyclo*butyldimethylcarbinol by the action of hydriodic (or hydrobromic) acid is probably effected by way of the stages:



$CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot CMe_2I \longrightarrow$



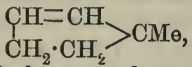
$\begin{matrix}CH_2\cdot CH\\ | \qquad | \\ CH_2\cdot CH\end{matrix}>CMe_2 \longrightarrow \begin{matrix}CH_2\cdot CHI\\ | \\ CH_2\cdot CH_2\end{matrix}>CMe_2$; both the bromide and iodide formed, when treated with alcoholic potassium hydroxide, yield 1 : 1-dimethyl-Δ^2-*cyclo*pentene, the structure of which is demonstrated by the formation of *aa*-dimethylglutaric acid on oxidation. The formation of 1 : 2-dimethyl-Δ^1-*cyclo*pentene by the action of hydriodic or hydrobromic acid on *cyclo*butyldimethylcarbinol probably proceeds as follows:



$$CH_2{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CH\cdot CHMe\cdot CH_2I \rightarrow CH_2{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}C{<}\begin{matrix}CHMe\\ \vert \\CH_2\end{matrix} \rightarrow CH_2{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CMe\cdot CHMeI \rightarrow \begin{matrix}CH_2\cdot CMe\\ \vert \quad\ \vert \\ CH_2\cdot CH\end{matrix}{>}CHMe \rightarrow \begin{matrix}CH_2\cdot CMeI\\ \vert \\ CH_2—CH_2\end{matrix}{>}CHMe \rightarrow CH_2{<}\begin{matrix}CH_2\cdot CMe\\ \Vert \\ CH_2\cdot CMe\end{matrix}.$$

The structure of this hydrocarbon, which is regarded as identical with Rénard's heptinene and with that obtained by Maquenne from perseitol (see this vol., i, 530), is deduced from the fact that it yields γ-acetobutyric acid on oxidation.

The action of hydrobromic acid on *cyclo*butyldimethylcarbinol yields: (1) 2-*bromo*-1 : 1-*dimethyl*cyclo*pentane*, $C_7H_{13}Br$, b. p. 167°/764 mm., D_0^{20} 1·2523, n^{20} 1·4797, which gives 1 : 1-dimethyl-Δ^2-*cyclo*pentene (*vide infra*) on treatment with alcoholic potassium hydroxide; (2) an unstable bromo-derivative, which yields 1 : 2-dimethyl-Δ^1-*cyclo*pentene when distilled in a current of steam.

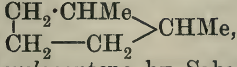
1 : 1-*Dimethyl*-Δ^2-cyclo*pentene*,  $\begin{matrix}CH{=}CH\\ \vert \\ CH_2\cdot CH_2\end{matrix}{>}CMe$, b. p. 78—78·5°/754 mm., D_0^{20} 0·7580, n^{20} 1·4190, has an odour resembling that of naphthalene, gives an intense green coloration when it is heated with concentrated sulphuric acid and alcohol added to the mixture, and yields *aa*-dimethylglutaric acid when oxidised with nitric acid.

The action of hydriodic acid on *cyclo*butyldimethylcarbinol also yields two products: (1) 2-*iodo*-1 : 1-*dimethyl*cyclo*pentane*, $C_7H_{13}I$, b. p. 98—99°/40 mm., D_0^{20} 1·5020, n^{20} 1·5240, which gives 1 : 1-dimethyl-Δ^2-*cyclo*pentene when treated with alcoholic potassium hydroxide; (2) an unstable iodo-derivative, which gives 1 : 2-dimethyl-Δ^1-*cyclo*pentene when distilled in a current of steam.

The reduction of 1 : 1-dimethyl-Δ^2-*cyclo*pentene by Sabatier's method, and the reduction of 2-iodo-1 : 1-dimethyl*cyclo*pentane by means of a zinc-copper couple, both yield 1 : 1-dimethyl*cyclo*pentane (compare Abstr., 1905, i, 772).

The reduction of 1 : 1-dimethyl-Δ^2-*cyclo*pentene by means of sulphuric acid yields 1 : 2-dimethyl*cyclo*pentane, which is also obtained, together with methyl*cyclo*hexane, when the reduction is effected by means of hydriodic acid. The reduction of 2-bromo-1 : 1-dimethyl*cyclo*pentane by hydriodic acid also yields a mixture of 1 : 2-dimethyl*cyclo*pentane and methyl*cyclo*hexane.

The oxidation of 1 : 2-dimethyl-Δ^1-*cyclo*pentene by means of nitric acid gives, as main products, acids such as oxalic and succinic, which are accompanied by a small proportion of a *compound*, $C_7H_{12}O_4N_2$, m. p. 202° (decomp.), the nature of which was not determined.

1 : 2-*Dimethyl*cyclo*pentane*,  $\begin{matrix}CH_2\cdot CHMe\\ \vert \\ CH_2—CH_2\end{matrix}{>}CHMe$, prepared by the reduction of 1 : 2-dimethyl-Δ^2-*cyclo*pentene by Sabatier's method, is a liquid, b. p. 92·7—93°/762 mm., D_0^{20} 0·7534, n^{20} 1·4126, which is

completely dissolved when heated with nitric acid (D 1·52), giving products which are under investigation. T. H. P.

Electro-Syntheses. III. Sima M. Losanitsch (*Ber.*, 1908, **41**, 2683—2688. Compare this vol., ii, 32).—In the apparatus previously described, benzene vapour alone, or mixed with other gases, is submitted to the silent electric discharge. Benzene alone gives a solid, insoluble in benzene; a liquid, soluble in ether or benzene; a solid, soluble in benzene, insoluble in ether. All three have the formula $C_{24}H_{25}$, and absorb oxygen. In presence of air, the resulting product is a dark, viscous substance containing nitrogen; with hydrogen, a yellow oil, $C_{28}H_{34}$, is obtained; with methane, a viscous, yellowish-red liquid, $C_{28}H_{36}$; with ethylene, a viscous, brownish-red liquid, $C_{28}H_{34}$; with acetylene, a yellowish-brown mass containing two substances, one soluble, the other insoluble, in benzene. Both have the composition $C_{48}H_{46}$, and absorb oxygen. The product with carbon monoxide is a dark viscous liquid, containing one substance soluble in ether, and a second, insoluble, which absorbs oxygen, yielding substances of the composition $C_{22}H_{22}O_2$ and $C_{20}H_{20}O_3$ respectively, and with carbon disulphide a dark solid, $C_8H_{10},6CS_2$.

The behaviour of ammonia, mixed with other gases, under the influence of the silent discharge has been examined. With an equal volume of ethylene, it yields a yellow basic oil, $C_{10}H_{21}N_3$, which absorbs oxygen; with acetylene, a dark red basic liquid, $C_{18}H_{30}N_4$, is formed, which absorbs oxygen; with benzene, a reddish-brown oily liquid, $C_{16}H_{24}N_2$, is formed, which absorbs oxygen.

In his answer to Loeb's criticisms (this vol., i, 117), the author states that the analyses of the preceding substances give concordant results only after the preparations have been saturated with oxygen by exposure to the air for about a month. C. S.

Syntheses by means of Sodium and Alkyl Halides. Paul Schorigin (*Ber.*, 1908, **41**, 2711—2717).—In continuation of his former work (Abstr., 1907, i, 753), the author has investigated the action of sodium and alkyl halides on ketones. Here, as before, it is probable that the sodium alkyl is formed as an intermediate product, for the corresponding tertiary alcohols (or their dehydration products) can be isolated from the products of reaction:

$$RNa + R'{\cdot}CO{\cdot}R'' = CRR'R''{\cdot}ONa.$$

In addition to this, several other reactions take place, for example, the formation of hydrocarbons, thus:

$$RNa + RX = R{\cdot}R + NaX,$$

and the formation of compounds of sodium with the ketones. The production of compounds of high b. p. also occurs, so that the yield of tertiary alcohols is low, varying from 5% to 10%.

The nature of the blue substances which are formed in the Fittig and Wurtz syntheses is discussed, and the author suggests that they may consist of a blue modification of sodium iodide or possibly salts of sodium quadrantoxide.

αα-Diphenyl-δ-methyl-Δ^α-amylene, $CPh_2{:}CH{\cdot}CH_2{\cdot}CHMe_2$, prepared by the action of sodium on a mixture of benzophenone and *iso*amyl bromide in ethereal solution, is a colourless liquid, b. p. 178°/16 mm., D_4^0 0·9907, D_4^{25} 0·9725, $n_D^{17 \cdot 8}$ 1·57463. It is not formed by the action of magnesium *iso*amyl bromide on benzophenone. When ethyl iodide is substituted for *iso*amyl iodide in the above reaction, diphenylethylcarbinol is produced. The interaction of sodium, acetophenone, and *iso*amyl iodide leads to the formation of *phenylmethyl*iso*amylcarbinol*, a colourless liquid, b. p. 135—137°/15 mm., D_4^0 0·9608, D_4^{20} 0·9450, n_D^{19} 1·50596.

When a stream of carbon dioxide is led through a mixture of sodium, benzene, and *iso*amyl bromide, a blue substance (referred to above) is produced, which is indifferent towards carbon dioxide, and, in addition, a small amount of benzoic acid is formed.

By the action of carbon dioxide on a mixture of sodium and *iso*butyl bromide in ethereal solution, a very small quantity of *iso*valeric acid is obtained. J. C. C.

Reduction of Nitro-compounds with Zinc Dust and Acetic Acid. GUSTAV HELLER (*Ber.*, 1908, 41, 2689—2692).—The discovery of a new step in the reduction of *o*-nitromandelonitrile by zinc dust and 33% acetic acid at a low temperature, whereby a double compound of a dihydroxylamino- and a hydroxylamino-derivative is produced (Abstr., 1906, i, 585; Heller and Sourlis, this vol., i, 208), has led the author to submit a number of other *o*-nitro-compounds to this process of reduction. It is remarkable that the presence of an ortho-substituent appears to favour the reduction, for, whilst *o*-nitromandelonitrile is readily reduced at 0°, nitrobenzene, even at the ordinary temperature, is scarcely attacked, yielding only a small amount of phenylhydroxylamine.

o-Nitrobenzaldehyde gives a solution containing *o*-aminobenzaldehyde and anthranil.

[With JULIUS SÖLLING.]—*o*-Nitrobenzoic acid, when reduced with zinc dust and 50% acetic acid in presence of sodium acetate at 35—40°, yields a mixture of benzidine-2 : 2′-dicarboxylic acid and azoxybenzoic acid; the latter is also produced when the reduction is carried on in ammoniacal solution. J. C. C.

Products of the Nitration of *o*-Chloronitrobenzene. IWAN OSTROMISSLENSKY (*J. pr. Chem.*, 1908, [ii], 78, 260—262).—According to Jungfleisch (*Ann. Chim. Phys.*, 1868, [iv], 15, 239), 1-chloro-2 : 4-dinitrobenzene, formed by nitration of chlorobenzene or of *o*-chloronitrobenzene, is obtained in a labile modification, m. p. 43°, and a stable modification, m. p. 50°. As the reduction products of these two modifications were found not to be identical, Beilstein considered (*Handbuch*, 3rd ed., II, 84) the labile form to be 1-chloro-2 : 6-dinitrobenzene, and states that this undergoes intramolecular change into the 1 : 2 : 4-isomeride when brought into contact with a crystal of the latter. As no other such transformation of a benzene derivative is known, the present author undertook a fresh study of the nitration of *o*-chloronitrobenzene, and has found that, whilst the main product is 1-chloro-2 : 4-dinitrobenzene, there is formed also 1-*chloro-*

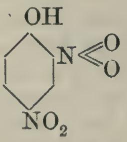
2 : 6-*dinitrobenzene*, $C_6H_3Cl(NO_2)_2$, which crystallises in needles, m. p. 38°, yields 2 : 6-dinitrophenol on treatment with warm concentrated potassium hydroxide, and is not identical with Jungfleisch's labile modification. G. Y.

Structure of Benzene. I. Polymorphic Modifications of Aromatic Compounds. II. Homogeneity of the ortho- and of the meta-Derivatives of Benzene. III. The Two Chemically Isomeric 2 : 4-Dinitrophenols. IWAN OSTROMISSLENSKY (*J. pr. Chem.*, 1908, [ii], 78, 263—279. Compare Abstr., 1907, i, 120, 596 ; preceding abstract).—It is found that both modifications of 1-chloro-2 : 4-dinitrobenzene, (1) on reduction with tin and hydrochloric acid or with stannous chloride (Claus and Stiebel, Abstr., 1887, 810), yield two chloronitroanilines, m. p. 117·8° and 101—102° ; (2) when treated with aniline, form 2 : 4 : 2′ : 4′-tetranitrodiphenylamine, m. p. 155—156°, and (3) on treatment with cold concentrated potassium hydroxide, are converted into 2 : 4-dinitrophenol, m. p. 113·2°. The two modifications are, therefore, chemically identical. Attempts to prepare two modifications of either of the chloronitroanilines were unsuccessful. It is suggested that Jungfleisch's chloronitroaniline, m. p. 89°, may be 2-chloro-3-nitroaniline, derived from 1-chloro-2 : 6-dinitrobenzene.

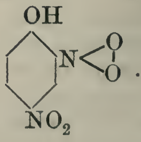
The existence of the liquid modification of 1-chloro-3 : 4-dinitrobenzene (Laubenheimer, this Journ., 1876, ii, 294) is confirmed. A mixture of the liquid and solid modifications is obtained when the solid modification is recrystallised from ether. The action of ammonia on the ethereal solution of this mixture leads to the formation of a *chloronitroaniline*, $C_6H_5O_3N_2Cl$, which crystallises in yellow prisms, melts when handled, has a blue fluorescence, is not identical with either of the known 3-chloro-6-nitro- and 4-chloro-6-nitro-anilines, and is probably a derivative of the liquid modification of 1-chloro-3 : 4-dinitrobenzene. It is considered that these cases of isomerism may depend on a difference in the structure of a nitro-group.

With the object of proving the homogeneity of the ortho- and of the meta-derivatives of benzene, *o*-chloronitro-, *m*-chloronitro-, *o*-dinitro-, 1-chloro-3 : 4-dinitro-, and 1-chloro-2 : 4-dinitro-benzene were subjected to fractional separation in the manner employed by Groos for the separation of the rare earths. The number of fractions obtained varied between 60 and 125. All the fractions of each substance were identical as to the m. p. and the crystalline constants.

The two modifications of 2 : 4-dinitrophenol are discussed, and it is suggested that here, also, the isomerism arises from a difference in the structure of a nitro-group, the two modifications having the constitutions :



and



G. Y.

Transformation of Phenylnitromethane [ω-Nitrotoluene] into Phenyldinitromethane [Di-ω-nitrotoluene]. Giacomo Ponzio (*Gazzetta*, 1908, 38, ii, 417—420).—*Phenyldibromonitromethane* [*Di-ω-bromo-ω-nitrotoluene*], $CPhBr_2\cdot NO_2$, prepared by the action of an alkaline solution of bromine on the sodium derivative of phenylnitromethane, is a colourless oil heavier than water, and has a pungent odour. On treatment with potassium hydroxide and potassium nitrite in alcoholic solution, it is converted into the potassium derivative of phenyldinitromethane; the reaction is possibly expressed by the equation:

$$CPhBr_2\cdot NO_2 + KNO_2 + 2KOH = CPhK(NO_2)_2 + 2KBr + H_2O + O,$$

the oxygen oxidising part of the alcohol (compare ter Meer, Abstr., 1876, 30, 185). Phenyldinitromethane is obtained from its potassium derivative by the action of dilute sulphuric acid. T. H. P.

Partial Electrolytic Reaction of Polynitro-compounds in the Presence of Vanadium Compounds. Hans Hofer and Fritz Jakob (*Ber.*, 1908, 41, 3187—3199).—The use in electrolytic reactions of inorganic compounds which are themselves reduced at the cathode, modifies the reduction of nitro-compounds. Vanadium, occurring as it does in so many forms of oxidation, gives a potential scale extending from the low oxidation potential of vanadic acid to the high reduction potential of bivalent vanadium salts. It should therefore be suitable for the partial reduction of polynitro-compounds, as it gives the necessary high potential (compare Brand and Zöller, Abstr., 1906, i, 80; 1907, i, 755).

The preliminary work consisted in measuring the potential of the various vanadium compounds, with the result: vanadic acid −1·17, vanadyl sulphate −0·76, vanadic sulphate −0·23 volt (e_h for mercurosulphate electrode −0·69 volt). From the Peters-Nernst formula, the "equilibrium potential" for mixtures of salts can be calculated, and the reduction tension determined.

The cathode was contained in a narrow beaker containing the vanadyl sulphate, sulphuric acid, alcohol, and the polynitro-compound; the lead anode was placed in a porous cell containing normal sulphuric acid at 50—60°.

2 : 4-Dinitrotoluene, with a platinum cathode and potential 0·03 volt, gave chiefly *p*-nitrotoluidine with tolylenediamine and 2 : 2′-dinitro-4 : 4′-azoxytoluene. With a potential of 0·10—0·15 volt, more of the azoxy-compound was produced. Lead and zinc are very much less suitable as cathodes; with copper, no azoxy-derivative was obtained, but some dinitrotoluene was recovered unchanged.

Platinum was used as electrode in the remaining experiments. 2 : 6-Dinitrotoluene gave 2 : 2′-dinitro-6 : 6′-azoxytoluene, 2-nitro-6-toluidine, and a little of the corresponding diamine. With 2 : 4 : 6-trinitrotoluene, only 2 : 6-dinitro-4-aminotoluene was obtained. It sinters at 108°, m. p. 127°, to a viscous liquid, which becomes mobile at 150° (Beilstein gives m. p. 168°: Abstr., 1880, 636); its constitution was determined by preparing 2 : 6-dinitrotoluene by digesting the diazo-compound with alcohol.

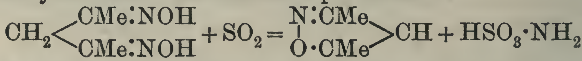
m-Dinitrobenzene gave *m*-nitroaniline, *m*-phenylenediamine, and the dinitroazoxybenzene; 2 : 4-dinitrophenol yielded *o*-nitro-*p*-aminophenol, and picric acid, picramic acid. W. R.

Simple Method of Preparing the Imides of the Aromatic Sulphonic Acids. TAMEMASA HAGA (*J. Coll. Sci. Tōkyō*, 1908, **25**, xiii, 1—30).—Very little work has been done hitherto on the aromatic sulphonimides (compare Farbwerke vorm. Meister, Lucius & Brüning, Abstr., 1902, i, 364). It is found that these compounds can be readily obtained by reducing aromatic sulphonylhydroxylamines, preferably with sulphur dioxide, thus: $(Ph\cdot SO_2)_2NOH + SO_2 + H_2O = (Ph\cdot SO_2)_2NH + H_2SO_4$. The following reaction also takes place to some extent at the same time:

$$4(Ph\cdot SO_2)_2NOH + H_2O = 2(Ph\cdot SO_2)_2NH + 4Ph\cdot SO_3H + N_2O.$$

This reaction proceeds in the absence of sulphur dioxide, for it is found that dibenzenesulphonylhydroxylamine in aqueous alcoholic solutions decomposes mainly according to the last equation, a small quantity of tribenzenesulphonylhydroxylamine also being formed. It is probable that the sulphonate, $(Ph\cdot SO_2)_2N\cdot SO_3H$, is formed as an intermediate product during the reduction of dibenzenesulphonylhydroxylamine with sulphur dioxide, but its existence could not be established. Dibenzenesulphonylhydroxylamine, when reduced with sodium amalgam, yields a quantity of benzenesulphinic acid, with liberation of ammonia; the yield of dibenzenesulphonimide is very small.

Krafft and Bourgois (Abstr., 1892, 700) have shown that an oximino-nitrogen atom attached to carbon alone becomes sulphonated when treated with sulphur dioxide, and is at the same time detached from the carbon. When, however, a compound containing two oximino-radicles united to two separate carbon atoms in the molecule is reduced with sulphur dioxide, only one of the nitrogen atoms is separated in the form of amidosulphonic acid; the other nitrogen atom remains united to carbon. For example, when acetylacetonedioxime in aqueous solution is treated with sulphur dioxide, it is converted into 3 : 5-dimethyl*iso*oxazole and amidosulphonic acid:



$$CH_2<\begin{matrix}CMe{:}NOH\\ CMe{:}NOH\end{matrix} + SO_2 = \begin{matrix}N{:}CMe\\ |\\ O\cdot CMe\end{matrix}>CH + HSO_3\cdot NH_2.$$

The non-removal of one of the nitrogen atoms is not due to the tendency of forming a ring compound, since acetonylacetonedioxime, when similarly treated, yields amidosulphonic acid and an oily *substance*, which still contains a nitrogen atom combined with carbon in a form capable of yielding hydroxylamine on hydrolysis.

Diphenylsulphonylhydroxylamine (dibenzenesulphohydroxamic acid) crystallises with 1Et·OH and sometimes with $2H_2O$; the anhydrous substance has m. p. 132°; Angeli, Angelico, and Scurti give m. p. 126° (Abstr., 1902 i, 765). *Dibenzenesulphonimide*, $(Ph\cdot SO_2)_2NH$, probably crystallises with $1\frac{1}{2}H_2O$; it forms thick prisms, and when anhydrous has m. p. 157°; the *barium*, $C_{24}H_{20}O_8S_4N_2Ba,2H_2O$, *mercuric*, $C_{24}H_{20}O_8S_4N_2Hg$, *potassium*, $C_{12}H_{10}O_4S_2NK$, *mercurous*, *silver*, *sodium*, and *ammonium* salts are described.

Di-o-tolylsulphonylhydroxylamine, $(C_6H_4Me\cdot SO_2)_2NOH$, prepared by the action of nitrous acid on *o*-toluenesulphinic acid, crystallises with $1H_2O$ in small prisms, m. p. 106—107°; it is converted by an excess of nitrous fumes evolved from arsenious oxide and nitric acid (D 1·32) into *tri-*o*-tolylsulphonylhydroxylamine*, $(C_6H_4Me\cdot SO_2)_3NO$, crystallising in small needles, m. p. 129·5°. *Di-*o*-toluenesulphonimide*,

$$(C_6H_4Me\cdot SO_2)_2NH,$$

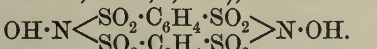
crystallises with H_2O in thick plates or short prisms; the anhydrous substance sinters at 178°, m. p. 184°; the *barium* salt,

$$(C_{14}H_{14}O_4NS_2)_2Ba,2H_2O,$$

forms minute needles.

*Di-*p*-toluenesulphonimide*, $(C_6H_4Me\cdot SO_2)_2NH$, forms crystals, m. p. 168—170°. W. H. G.

Oximes and Imides of Benzenedisulphonic Acids. TSUNEO SUZUKI (*J. Coll. Sci. Tōkyō*, 1908, **25**, xiv, 1—21).—Mol.-wt. determinations show that the substance described by Autenrieth and Hennings as *m*-benzenedisulphonylhydroxamic acid, $C_6H_4{:}(SO_2)_2{:}NOH$ (compare Abstr., 1902, i, 389), is bimolecular, and probably has the formula



$$OH\cdot N{<}{\begin{smallmatrix}SO_2\cdot C_6H_4\cdot SO_2\\SO_2\cdot C_6H_4\cdot SO_2\end{smallmatrix}}{>}N\cdot OH.$$

It crystallises with alcohol, $[C_6H_4(SO_2)_2NOH]_2,1\frac{1}{2}EtOH$, and with acetone,

$$[C_6H_4(SO_2)_2NOH]_2,\tfrac{2}{3}COMe_2.$$

When reduced by sulphur dioxide, it yields *m-benzenedisulphonimide*, $NH(SO_2\cdot C_6H_4\cdot SO_2)_2NH$, crystallising in prisms with $2H_2O$; the *potassium* ($1\frac{1}{2}H_2O$), *sodium* ($6H_2O$), *silver*, and *potassium silver* salts are described.

p-*Benzenedisulphonehydroxamic acid* (p-*benzenedisulphonylhydroxylamine*), $NOH(SO_2\cdot C_6H_4\cdot SO_2)_2NOH$, prepared by the action of nitrous acid on *p*-benzenedisulphinic acid, crystallises with $1\frac{1}{2}COMe_2$ in thin plates, and decomposes suddenly at 210°.

p-*Benzenedisulphonimide*, $NH(SO_2\cdot C_6H_4\cdot SO_2)_2NH$, crystallises with $2H_2O$ in colourless prisms; the *sodium*, *potassium*, *silver*, and *mercurous* salts are described.

p-*Bromo-*o*-benzenedisulphonylhydroxamic acid*, $C_6H_3Br(SO_2)_2{:}NOH$, crystallises in prisms, and decomposes at 82°; it is reduced by sulphur dioxide to the corresponding *sulphonimide*.

o-*Benzenedisulphonylhydroxamic acid* crystallises in colourless prisms, and decomposes at 45°; when reduced, it yields a *sulphonimide*.

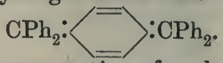
The benzenedisulphonehydroxamic acids described above are converted by cold fuming nitric acid into the corresponding sulphonimides, and are decomposed by aqueous ammonia, yielding ammonium salts of the corresponding disulphinic acids, thus:

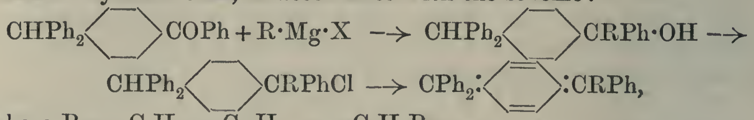
$$C_6H_4(SO_2)_2{:}NOH + 3NH_3 \longrightarrow C_6H_4(SO_2NH_4)_2 + N_2 + H_2O.$$

Ammonium m-*benzenedisulphinate*, $C_6H_4(SO_2NH_4)_2,H_2O$, crystallises in star-like clusters of elongated tetrahedra, m. p. 113—115°; the *silver* salt, $C_6H_4(SO_2Ag)_2$, is crystalline. *Ammonium* p-*benzenedisulphinate*, $C_6H_4(SO_2NH_4)_2,H_2O$, crystallises in slender needles, and decomposes at about 200°; the *silver* salt is amorphous. W. H. G.

[Coloured and Colourless Triphenylmethyl.] BERNHARD FLÜRSCHEIM (*Ber.*, 1908, **41**, 2746—2747).—Schmidlin's equilibrium formula, $CPh_3\cdot CPh_3 \rightleftarrows CPh_3$, for triphenylmethyl (this vol, i, 623) has been already suggested by the author (Abstr., 1905, i, 614).

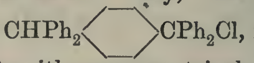
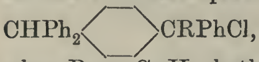
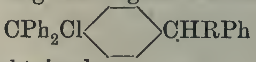
C. S.

Preparation of Hydrocarbons of the Quinodimethane Series and their Derivatives. Alexei E. Tschitschibabin (*Ber.*, 1908, **41**, 2770—2778. Compare Thiele and Balhorn, Abstr., 1904, i, 491; Staudinger, this vol., i, 410, 411).—The tendency of *p*-benzhydryltriphenylmethyl chloride or bromide to acquire an orange colour (this vol., i, 624) is due to the ready elimination of hydrogen halide with the formation of tetraphenylquinodimethane,  This reaction leads to a convenient method for the preparation of such coloured hydrocarbons, in accordance with the scheme:



where $R = p\text{-}C_7H_7$, $\alpha\text{-}C_{10}H_7$, or $p\text{-}C_6H_4Br$.

The elimination of the halogen acid occurs slightly at the ordinary temperature, but is best effected by quinoline in hot xylene in an atmosphere of carbon dioxide.

The converse operation, the addition of the halogen acid to the quinodimethane hydrocarbon, proceeds readily, resulting in the formation of the original halide,  in the case of tetraphenylquinodimethane, whilst with unsymmetrical hydrocarbons the addition takes place in two directions, yielding the original halide,  or the isomeride, ; when $R = \alpha\text{-}C_{10}H_7$, both additive products are obtained.

Tetraphenylquinodimethane has the properties described by Thiele and Balhorn and by Staudinger (*loc. cit.*). The m. p. in a sealed capillary tube filled with carbon dioxide is 268° (partial decomp.). The addition of hydrogen chloride or bromide is effected by treating a solution of the hydrocarbon in hot benzene with the hydrogen halide, dissolved in glacial acetic acid, in an atmosphere of carbon dioxide.

p-Benzhydryltriphenylmethyl bromide does not melt at 140° as given (Tschitschibabin, *loc. cit.*), but decomposes gradually above 200°.

The reaction between magnesium α-naphthyl bromide and *p*-benzoyltriphenylmethane in ether leads, after the usual operations, to the formation of a viscous oil, which is converted by hydrogen chloride in glacial acetic acid into p-*benzhydryldiphenyl-α-naphthylmethyl chloride*, $CHPh_2\cdot C_6H_4\cdot CPhCl\cdot C_{10}H_7$, m. p. 129—130°, from which *triphenyl-α-naphthylquinodimethane*, $CPh_2\colon C_6H_4\colon CPh\cdot C_{10}H_7$, is obtained. The hydrocarbon has m. p. 240—241° (in carbon dioxide), forms intensely orange-red crystals, and, like the chloride, dissolves in concentrated sulphuric acid with a green or violet-red colour, according to the concentration of the solution. The dry hydrocarbon is stable in air, but oxidises readily in solution. The addition of hydrogen chloride results mainly in the formation of p-*phenyl-α-naphthylmethyltri-*

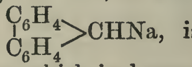
phenylmethyl chloride, $CPh_2Cl\cdot C_6H_4\cdot CHPh\cdot C_{10}H_7$, m. p. 174—175° (decomp.).

p-*Benzhydryldiphenyl*-p-*tolylmethyl bromide*,

$CHPh_2\cdot C_6H_4\cdot CPhBr\cdot C_7H_7$,

m. p. 156—164° (decomp.), is a yellow powder. *Triphenyl*-p-*tolylquinodimethane*, $CPh_2{:}C_6H_4{:}CPh\cdot C_7H_7$, m. p. 197° (in carbon dioxide), forms orange-red crystals, develops an orange colour in sulphuric acid, and is very sensitive to oxygen or light when incompletely dried. p-*Bromotetraphenylquinodimethane*, $CPh_2{:}C_6H_4{:}CPh\cdot C_6H_4Br$, m. p. 257—259° (decomp.) in carbon dioxide, is a brownish-red, crystalline powder; it dissolves in sulphuric acid to an orange-red solution.

C. S.

Sodium Derivative of Fluorene. RUDOLF WEISSGERBER (*Ber.*, 1908, **41**, 2913—2916).—The reaction between fluorene and sodium or sodamide occurs at much lower temperatures than with potassium hydroxide (Abstr., 1901, i, 521). When fluorene is heated with the calculated amount of sodamide at 120°, and finally at 150°, or with sodium at 180—200°, the *sodium* derivative,  $\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right>CHNa$, is obtained as a hard, yellowish-brown, crystalline mass, which is decomposed by water, yielding fluorene and sodium hydroxide; bisdiphenylene-ethane is formed as a by-product. The same reaction occurs when dry ammonia is passed into fused sodium and fluorene at 150°, but in this case the by-products are very small. C. S.

Structure of Retene. PAUL LUX (*Monatsh.*, 1908, **29**, 763—777).—It has been stated by Fortner (Abstr., 1904, i, 729) that retene is either 2-methyl-8-propyl- or 8-methyl-2-propyl-phenanthrene. This conclusion is confirmed by the present author, who finds that when retene ketone or retenequinone is fused with potassium hydroxide, a methyl*iso*propyldiphenyl-2-carboxylic acid is formed; the position of the carboxyl group is decided by the fact that the acid cannot be esterified; hence one of the side-chains in retene is in the ortho-position to the CH:CH group. At the same time a small amount of an *iso*propyldiphenyldicarboxylic acid is produced; as this readily yields a neutral ester, it is probably either 4-*iso*propyldiphenyl-2 : 3′- or 3-*iso*propyldiphenyl-2′ : 4′-dicarboxylic acid.

Dimethyl fluorenonedicarboxylate, m. p. 188—189° (corr.) (Bamberger and Hooker, Abstr., 1885, 906, give m. p. 184°), when partly hydrolysed, furnishes an *acid* ester, m. p. 260—261° (corr.), and by partly esterifying the dicarboxylic acid a second *acid* ester, m. p. 275—277° (corr.), is obtained. The *silver* salt of the first ester, on distillation in a vacuum, gives methyl fluorenone-2-carboxylate, m. p. 186—187° (corr.) (Fortner gives 181°), and the *silver* salt of the second ester yields the same compound, so that apparently an interchange of silver and methyl takes place; hence the constitution of the two acid esters cannot be decided from these data, and the intended preparation of fluorenone-1- and -2-carboxylic acids could not be effected.

Reteneglycollic acid is produced when retenequinone is boiled with

10% methyl-alcoholic potash; the *methyl* ester has m. p. 112—113° (corr.).

*Methyl*iso*propyldiphenyl-2-carboxylic acid*,

$$C_6H_4Pr^{\beta}(\text{or Me})\cdot C_6H_3Me(\text{or }Pr^{\beta})\cdot CO_2H,$$

prepared by fusing a mixture of retenequinone (or retene ketone) and lead peroxide with potassium hydroxide, crystallises in octahedra, m. p. 132—134° (corr.); the *silver* salt was analysed. By treating the acid with thionyl chloride, or by distilling it with lime or its barium salt with sodium methoxide, retene ketone is produced. On distilling the silver salt in a current of hydrogen, the acid passes over.

4-iso*Propyldiphenyl*-2 : 3′-*dicarboxylic acid* (or 3-iso*propyldiphenyl*-2′ : 4′-*dicarboxylic acid*) has m. p. 247—249° (corr.); the *methyl* ester is a white, microcrystalline powder, m. p. 93—95° (corr.); the *silver* salt was analysed. J. C. C.

Nitration of Aniline and its Derivatives. OTTO N. WITT and ERHARD WITTE (*Ber.*, 1908, 41, 3090—3097).—In continuation of the investigation of Witt and Utermann (compare Abstr., 1907, i, 27), the effect produced by using a very large excess of strong mineral acids during the nitration of aniline has been studied. Both *o*- and *p*-nitroaniline, dissolved in concentrated sulphuric acid (monohydrate), are converted by a mixture of concentrated sulphuric and nitric acids (prepared by adding dry potassium nitrate to the sulphuric acid), at temperatures below 5°, into picramide, the yield being between 58% and 67% of the theoretical, and trinitrophenylnitramic acid. Picramide may also be prepared in a similar manner from acetanilide, the yield being 67% of the theoretical.

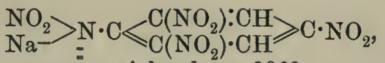
m-Nitroaniline is converted by the nitric-sulphuric acid mixture into tarry products, but *m*-nitroacetanilide under the same treatment yields 3 : 4-dinitroacetanilide; if the action is allowed to proceed for several days, this substance undergoes further nitration, forming 3 : 4 : 6-trinitroaniline.

The conclusion drawn by Martinsen (Abstr., 1905, ii, 149), that only 67% of the *p*-nitroaniline is converted into picramide because of a simultaneous sulphonation of the *p*-nitroaniline, is thus shown to be incorrect, since the remainder is converted into trinitrophenylnitramic acid; further, picramide is not best prepared by the nitration of aniline in the presence of sulphuric acid, as stated by this author, since the *m*-nitroaniline formed together with the ortho- and para-isomerides would not be converted into picramide.

Picramide acetate, $C_8H_4O_7N_4$, prepared by adding one drop of concentrated sulphuric acid to a solution of picramide in acetic anhydride, forms colourless needles, which commence to decompose at 207°, m. p. about 230°.

The following additive compounds of picramide (compare Mertens, Abstr., 1878, 725) are prepared by boiling equivalent quantities of the constituents dissolved in acetic acid. *Picramide α-naphthylamine*, $C_6H_4O_6N_4,C_{10}H_9N$, crystallises in dark red needles, having a metallic lustre; the *β-naphthylamine additive* compound forms red crystals.

Picramide α-naphthol, $C_6H_4O_6N_4,C_{10}H_8O$, crystallises in scarlet needles; the *β-naphthol* isomeride crystallises in red needles.

Sodium trinitrophenylnitramate,  $\begin{matrix}NO_2\\Na-\end{matrix}\!>\!N\cdot C\!<\!\begin{matrix}C(NO_2){:}CH\\C(NO_2)\cdot CH\end{matrix}\!>\!C\cdot NO_2$, crystallises in yellow needles, and decomposes violently at 203°.

3 : 4 : 6-*Trinitroaniline*, $C_6H_4O_6N_4$, crystallises in pale yellow needles. W. H. G.

Reduction of Aromatic Nitro-compounds by Sodium Sulphide.

Jan J. Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 42—43. Compare Abstr., 1900, i, 226, 482; 1901, i, 246, 460, 461).—The author has shown previously that when sodium disulphide acts on aromatic nitro-compounds containing halogen atoms or nitro-groups, the latter, when in the ortho- or para-position to a nitro-group, are replaced by the group S_2, forming disulphides. When no such atoms or groups are present, amino-compounds are formed together with small amounts of azoxy-compounds. It is now found that, when reduced with sodium disulphide in alcoholic solution, nitrobenzene, *o*- and *m*-nitrotoluenes, *o*-, *m*-, and *p*-nitroanisoles, *m*-chloro- and -bromo-nitrobenzenes, and 3 : 5-dichloro- and -dibromo-nitrobenzenes give a 70% yield of the corresponding amines. In the case of *o*- and *p*-chloronitrobenzenes, where the halogen atom is replaced by the group S_2, small amounts of *o*- and *p*-chloroanilines are formed. *p*-Nitrotoluene gives *p*-aminobenzaldehyde in addition to *p*-toluidine. By partial reduction, 3 : 5-dinitrotoluene furnishes 5-nitro-*m*-toluidine, 3 : 5-dinitroanisole gives 5-nitro-*m*-anisidine, 2 : 4-dinitroanisole (or phenetole) yields 4-nitro-*o*-anisidine (or phenetidine), and 1 : 3 : 5-trinitrobenzene gives 3 : 5-dinitroaniline. A small quantity of the azoxy-compounds is also usually produced. J. C. C.

Preparation and Constitution of Sulphoxides and Disulphoxides.

Oscar Hinsberg (*Ber.*, 1908, 41, 2836—2839).—Organic sulphides are converted by hydrogen peroxide into sulphoxides; disulphides under similar conditions take up two oxygen atoms, forming disulphoxides. This reaction has been proved to occur in the case of benzyl, phenyl, and β-naphthyl disulphides. Reasons are stated for adopting the formula R·SO·SO·R for the disulphoxides.

pp-*Diacetyldiaminodiphenyl sulphoxide*, $SO(C_6H_4\cdot NHAc)_2$, crystallises in small plates, m. p. 278°. The conversion of disulphide into disulphoxide is best carried out in cold acetic acid solution, using an excess of 3% hydrogen peroxide. E. F. A.

Compounds of Cobaltinitrites with *p*-Toluidine, Diazoaminotoluene, Hydrazine, and Nitrosohydrazine.

Karl A. Hofmann and Karl Buchner (*Ber.*, 1908, 41, 3084—3090).—It has been shown by Hofmann and Burger (Abstr., 1907, i, 751) that ammonium cobaltinitrite and ethylammonium cobaltinitrite decompose when heated, the component parts interacting in a normal manner. Such reactions between the nitrite group of the complex and that part of the salt outside the complex are of great interest, in that they throw light on the mode of union of the latter with the complex; further, since the nitrite group attached to the cobalt atom is not very reactive, the formation of substances was to be expected, which would ordinarily be produced so rapidly as intermediate products when free nitrous acid is employed as to render their isolation impossible.

p-Toluidine reacts with sodium cobaltinitrite in aqueous-alcoholic solution containing acetic acid, yielding diazoaminotoluene and *p-toluidine tetranitrito-bis-p-toluidinocobaltiate*, $[N_4O_8Co(C_7H_9N)_2]H,C_7H_9N$, crystallising in brownish-red, pointed, compact prisms. It is converted by alcoholic ammonia into ammonium cobaltinitrite, with elimination of *p*-toluidine. It is stable at the ordinary temperature, but decomposes when its aqueous solution is boiled, yielding nitrocresol with evolution of nitrogen.

In the absence of acetic acid, *p*-toluidine reacts with sodium cobaltinitrite, forming *nitritoaquo-bis-diazoaminotoluene cobalt*,

$$[NO_2Co(H_2O)(C_{14}H_{15}N_3)_2],$$

which crystallises in glistening, black, thick, rhombic plates or pyramids. It is very stable towards acids and alkalis, being attacked by these only at high temperatures.

Hydrazine unites with sodium cobaltinitrite in solutions containing small quantities of acetic acid, yielding *sodium diammonium cobaltinitrite*, $[Co(NO_2)_6]NaN_2H_6$, which forms yellow, rectangular crystals. It decomposes with evolution of two atoms of nitrogen when its aqueous solution is heated, and does not explode when heated alone. It loses $2H_2O$ when kept for some time over concentrated sulphuric acid, yielding *sodium nitrosohydrazine cobaltinitrite* (*sodium nitrosohydrazinetetranitritocobaltiate*), $[N_4O_8Co(NO\cdot NH)_2]Na$, obtained as glistening, dark purplish-violet crystals.

Hydroxodinitritohydrazine cobalt, $[HO(N_2O_4)Co(N_2H_4)NH_2]_2$, is formed by the action of an alkaline solution of hydrazine on sodium cobaltinitrite. It forms aggregates of dark purplish-red needles, decomposes violently when heated, and liberates nitrogen when boiled with water. W. H. G.

Derivatives of 2-Iodo-*p*-toluidine and 2-Iodo-4-nitrobenzoic Acid containing Uni- and Ter-valent Iodine. Conrad Willgerodt and Rudolf Gartner (*Ber.*, 1908, 41, 2813—2826).—I. *2-Iodo-p-toluidine and its Derivatives.*—*2-Iodo-p-toluidine*, $C_6H_3MeI\cdot NH_2$, prepared by reducing 2-iodo-*p*-nitrotoluene with ferrous sulphate in ammoniacal solution, crystallises in large, white needles, m. p. 37°; the *hydrochloride*, long, rather dark needles, the *sulphate*, shining leaflets, the *nitrate*, well-formed rhombs, and the *oxalate*, small rhombs, are described. *2-Iodoaceto-p-toluidide*, $C_6H_3MeI\cdot NHAc$, prepared from the base and acetic anhydride, forms white needles, m. p. 130°. *2-Iodo-p-tolylcarbamide*, $C_6H_3MeI\cdot NH\cdot CO\cdot NH_2$, forms well-defined rhombs, m. p. 194°; the N-*nitroso*-derivative,

$$C_6H_3MeI\cdot N(NO)\cdot CO\cdot NH_2,$$

crystallises in yellow, shining needles, which soon turn brown and decompose in the air, m. p. 99° (decomp). *Aceto-p-toluidide o-iodochloride*, $C_6H_3Me(ICl_2)\cdot NHAc$, prepared by passing chlorine into a glacial acetic acid solution of 2-iodoaceto-*p*-toluidide to which chloroform is added, forms yellow needles, decomposing at 100°. It was not found possible to prepare 2-iodoso- or 2-iodoxy-aceto-*p*-toluidide. An aqueous solution of *phenyl*-p-*acetylaminotolyliodonium hydroxide*,

$$C_6H_5\cdot I(OH)\cdot C_6H_3Me\cdot NHAc,$$

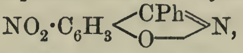
is obtained by the interaction of the iodochloride and mercury diphenyl; the *iodide*, pale yellow needles, m. p. 145°, the *bromide*, white prisms, m. p. 159·5—160°, the *dichromate*, yellow needles, becoming reddish-brown when dry and decomposing at 80°, and the *platinichloride*, small, yellow crystals, m. p. 125° (decomp.), are described.

II. 2-*Iodo*-4-*nitrobenzoic acid and its Derivatives.*—2-*Iodo*-4-*nitrobenzoic acid*, prepared by oxidising 2-iodo-*p*-nitrotoluene with nitric acid under pressure, forms long, pale yellow needles, m. p. 142°; the *silver* salt, white needles, *barium* salt,

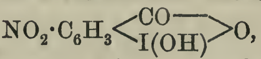
$$(NO_2\cdot C_6H_3I\cdot CO_2)_2Ba,H_2O,$$

methyl ester, long needles, m. p. 89°, and *ethyl* ester, large, shining prisms, m. p. 44°, are described. 2-*Iodo*-4-*nitrobenzoyl chloride* forms yellow needles, b. p. 196°/18 mm.; the *amide* forms yellow, rhombic crystals, m. p. 205°. The interaction of 2-iodo-4-nitrobenzoyl chloride, benzene, and aluminium chloride in presence of a small quantity of light petroleum leads to the formation of 2-*iodo*-4-*nitrobenzophenone*,

$$NO_2\cdot C_6H_3I\cdot COPh,$$

which forms aggregates of small needles, m. p. 90—91°; on heating with hydroxylamine hydrochloride and a little alcohol under pressure, there is formed the *oxime* in small prisms, m. p. 161—161·5°. This, when boiled with 50% aqueous sodium hydroxide, is condensed to 5-*nitrophenylindoxazen*,  $NO_2\cdot C_6H_3{<}\substack{CPh\\ O}{>}N$, which forms small rhombs, m. p. 139°. 4-*Nitrobenzoic acid* 2-*iodochloride*,

$$NO_2\cdot C_6H_3(ICl_2)\cdot CO_2H,$$

prepared by the action of chlorine on a chloroform solution of 2-iodo-4-nitrobenzoic acid, forms yellow needles; on warming with 10% aqueous sodium hydroxide, it is converted into 2-*iodoso*-4-*nitrobenzoic acid*, $NO_2\cdot C_6H_3(IO)\cdot CO_2H$ or  $NO_2\cdot C_6H_3{<}\substack{CO\\ I(OH)}{>}O$, which is also formed in small amount by treating 2-iodo-4-nitrobenzoic acid with fuming nitric acid. This acid crystallises in white needles, the m. p. of which varies with different preparations; the m. p.'s 190°, 196°, and 201° were observed. It can be crystallised unchanged from formic acid, and, when boiled with aqueous sodium hydroxide and alcohol, is decomposed with formation of iodic, 2-iodo-4-nitrobenzoic, and 4-nitrobenzoic acids. The *sodium* salt, brown leaflets, *silver* salt, small needles, *barium* salt, yellow needles, *copper* salt, bright green, amorphous precipitate, and *lead* salt, yellow powder, are described. Methyl 2-iodo-4-nitrobenzoate, when treated with chlorine in chloroform solution, yields *methyl*-4-*nitrobenzoate*-2-*iodochloride* as a pale yellow, crystalline precipitate, which, under the action of sodium hydroxide or carbonate, gives 2-iodoso-4-nitrobenzoic acid. The *methyl* ester of 2-iodoso-4-nitrosobenzoic acid was finally prepared by the action of hydrogen chloride on a methyl-alcoholic solution of 2-iodoxy-4-nitrobenzoic acid (see below); it crystallises in small needles, m. p. 180—181°.

2-*Iodoxy*-4-*nitrobenzoic acid*, $NO_2\cdot C_6H_3(IO_2)\cdot CO_2H$, prepared by oxidising the iodoso-acid with potassium permanganate in sulphuric acid solution, or, better, with sodium hypochlorite, forms white needles, m. p. 205° (mild explosion); the *silver* salt, small needles, which explode on heating, and the *lead* salt, bright yellow powder, are described.

III. *Preparation of* 2-*Iodo*-4-*aminobenzoic Acid.*—2-*Iodo*-4-*acetylaminobenzoic acid*, prepared by oxidising 2-iodoaceto-*p*-toluidide with potassium permanganate with the addition of magnesium sulphate, forms needles, m. p. 213—214°. On hydrolysis with concentrated hydrochloric acid, it yields 2-*iodo*-4-*aminobenzoic acid*, crystallising in needles, m. p. 180° (decomp.), which can also be obtained by reducing 2-iodo-4-nitrobenzoic acid with stannous chloride and hydrochloric acid; the *hydrochloride*, well-formed prisms, the *silver* salt, small, white needles, and the *methyl* ester, needles, m. p. 112°, are described.

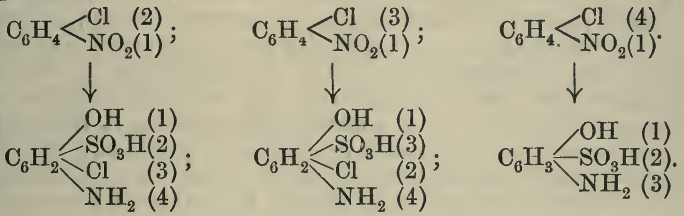
J. C. C.

Quaternary Phenacylammonium Salts. EDGAR WEDEKIND (*Ber.*, 1908, **41**, 2802—2805).—Quaternary phenacylammonium salts are obtained when one molecule of a tertiary base is allowed to act on one molecule of ω-bromoacetophenone at the ordinary temperature, care being taken that when the bromide is dissolved in the tertiary base the temperature does not exceed 30—40°.

Phenacylphenyldimethylammonium bromide (Abstr., 1902, i, 278) sinters between 100° and 110°, and decomposes between 115° and 125°. By shaking with moist silver oxide, it yields the corresponding *base*, from which the *platinichloride*, small, yellow prisms, and the *aurichloride* were prepared. *Phenacylphenylbenzylmethylammonium bromide* crystallises in fine, colourless needles, which decompose at 149—150°. *Phenacylphenylmethylethylammonium bromide* forms crystals, decomposing at 145°; the d-*bromocamphorsulphonate* is not suitable for experiments on resolving the substance, and no resolution could be effected by means of the d-*camphorsulphonate*. The latter forms small, colourless crystals, decomposing at 176°. J. C. C.

Phenylcarbylamine from Pyrogallol and Nitrobenzene. HEINRICH BRUNNER and V. VUILLEUMIER (*Chem. Zentr.*, 1908, ii, 588; from *Schweiz. Woch. Chem. Pharm.*, 1908, **46**, 436).—When a few drops of nitrobenzene are heated with a small quantity of pyrogallol in an aqueous alkaline solution, the characteristic odour of phenylcarbylamine is strongly developed. In alcoholic solution, the reaction proceeds differently, ammonia being evolved and no formation of carbylamine taking place. If, however, the product is treated with ether and fractionated in a vacuum, carbylamine may be isolated. The use of catechol instead of pyrogallol, leads to the formation of only a trace, whilst with resorcinol, quinol, phloroglucinol, and hydroxyquinol, carbylamine is not produced. *o*-, *m*-, and *p*-Chloro- and bromonitrobenzenes and *o*- and *m*-nitrotoluenes give carbylamine, but nitromethane, nitroethane, nitropropane, dinitrobenzene, *o*- and *p*-nitrophenols, *β*-naphthol, and *p*-nitrotoluene liberate ammonia, and do not give carbylamine. J. V. E.

p-**Aminophenolsulphonic Acid.** Heinrich Brunner and V. Vuilleumier (*Chem. Zentr.*, 1908, ii, 587—588; from *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 434—436).—When nitrobenzene is heated alone with sulphuric acid at 225°, there is obtained a small quantity of *p*-aminophenolsulphonic acid. In a similar manner, when resorcinol, quinol, catechol, pyrogallol, glycerol, mannitol, or dextrose is heated with nitrobenzene and sulphuric acid, 4-aminophenol-2-sulphonic acid is produced. This may be explained by an oxygen atom of the nitrobenzene wandering to the para-position, and then reduction occurring by the sulphur dioxide produced from the sulphuric acid and phenol. This view is supported by the fact that nitrobenzene, when heated with carbon and sulphuric acid, yields *p*-aminophenolsulphonic acid. Wandering of oxygen appears to be a common property of the nitro-group, as is indicated by the following observed changes which take place:



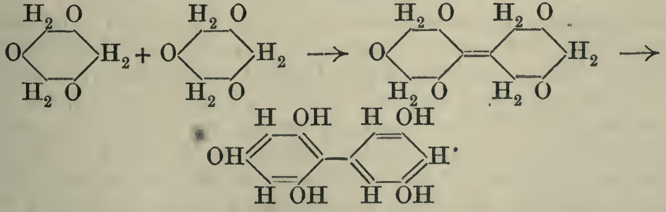
$$\begin{array}{ccc} C_6H_4{<}\begin{array}{l}Cl\ \ (2)\\ NO_2(1)\end{array}; & C_6H_4{<}\begin{array}{l}Cl\ \ (3)\\ NO_2(1)\end{array}; & C_6H_4{<}\begin{array}{l}Cl\ \ (4)\\ NO_2(1)\end{array}. \\ \downarrow & \downarrow & \downarrow \\ C_6H_2\begin{array}{l}OH\ \ \ (1)\\ SO_3H(2)\\ Cl\ \ \ \ (3)\\ NH_2\ (4)\end{array}; & C_6H_2\begin{array}{l}OH\ \ \ (1)\\ SO_3H(3)\\ Cl\ \ \ \ (2)\\ NH_2\ (4)\end{array}; & C_6H_3\begin{array}{l}OH\ \ \ (1)\\ SO_3H(2).\\ NH_2\ (3)\end{array} \end{array}$$

The corresponding bromo-derivatives behave in a similar manner.

J. V. E.

Picrates. Otto Anselmino (*Ber.*, 1908, 41, 2996).—When picric acid or yellow ammonium picrate is dissolved in 10% ammonium hydroxide at 80°, and crystallisation is induced at a higher temperature, a red modification of ammonium picrate, $C_6H_6O_7N_4$, is obtained, which appears to be stable when kept, but reverts to the yellow form on recrystallisation (compare Suida, this vol., i, 523). C. S.

Phloroglucide. Joseph Herzig and Richard Kohn (*Monatsh.*, 1908, 29, 677—688).—The ease with which phloroglucide is formed from 2 mols. of phloroglucinol by loss of 1 mol. of water under the



influence of concentrated sulphuric acid suggests that the glucide is an anhydride of the glucinol. Herzig, however, found (Abstr., 1899, i, 31) that phloroglucide forms a penta-acetyl derivative, and considered that the two phloroglucinol residues must be united by a carbon linking. A further study of phloroglucide has now confirmed the presence of the five hydroxyls, and it is suggested that the formation of the glucide may take place according to the preceding scheme.

When treated with diazomethane in ethereal solution, or with methyl sulphate and potassium hydroxide, phloroglucide forms a *pentamethyl ether*, $C_{12}H_5(OMe)_5$, which separates from alcohol in white crystals, m. p. 117—120°. The *monomethyl ether*, $C_{12}H_9O_4{\cdot}OMe$, prepared by the action of hydrogen chloride on the glucide in methyl-alcoholic solution, has m. p. 222—225°, yields the preceding pentamethyl ether on treatment with diazomethane, and, when boiled with acetic anhydride and sodium acetate, forms a *tetra-acetyl* derivative, $OMe{\cdot}C_{12}H_5(OAc)_4$, which is obtained in colourless crystals, m. p. 102—105°. The *monoethyl ether*, $C_{12}H_9O_4{\cdot}OEt$, has m. p. 165—168°.

Pentabromophloroglucide, $C_{12}Br_5(OH)_5$, formed by treating phloroglucide with bromine in glacial acetic acid or dichloroethylene solution, separates from ethyl acetate in colourless crystals, m. p. 242—245°, yields with diazomethane a *pentamethyl ether*, $C_{12}Br_5(OMe)_5$, m. p. 200—202°, and, when boiled with acetic anhydride and sodium acetate, forms a *penta-acetyl* derivative, $C_{12}Br_5(OAc)_5$, m. p. 198—202°.

Bromination of pentamethylphloroglucide in dichloroethylene solution leads to the formation of a *tetrabromo*-derivative, $C_{12}HBr_4(OMe)_5$, which separates from ethyl acetate in colourless crystals, m. p. 228—229°.

The tautomeric nature of phloroglucide appears in that, whilst the bromine of the pentabromophloroglucide is eliminated quantitatively by means of potassium hydroxide, the brominated ethers are stable under the same conditions. The results of a study of the hydrolysis of the tetra-acetyl derivative of monomethylphloroglucide by means of sulphuric acid show that with very dilute acid the four acetoxyls are hydrolysed completely, but that with increasing concentration of the acid there appears a condensation in which one acetyl group takes part; this reaction is smoothest when the proportion of acid to water present is 3 : 1. G. Y.

Aurin Dimethyl Ether. JOSEF HERZIG (*Monatsh.*, 1908, **29**, 653—659. Compare Baeyer and Villiger, Abstr., 1902, i, 769).—Aurin is readily methylated by diazomethane, although not by other common methylating agents, yielding *aurin dimethyl ether*,

$$C_{19}H_{12}O(OMe)_2,$$

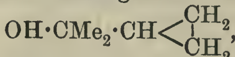
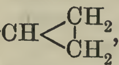
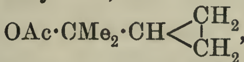
which crystallises in orange needles, m. p. 183—186°, is soluble in aqueous alkalis, and, when recrystallised from dilute hydrochloric acid, is converted into a *hydrate*, $C_{21}H_{18}O_3,H_2O$; this forms red crystals, m. p. 57—65°, and loses H_2O at 110°, forming again the dimethyl ether, m. p. 183—186°. Whilst aurin is readily acetylised, forming triacetylaurincarbinol, aurin dimethyl ether reacts only with difficulty with acetic anhydride alone or in presence of sodium acetate, but, on treatment with the anhydride and sulphuric acid, it yields a white *product*, which, on recrystallisation from alcohol, forms the *acetyl* derivative, *acetoxydimethoxytriphenylcarbinyl ethyl ether*,

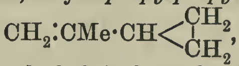
$$OAc{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}OMe)_2{\cdot}OEt,$$

crystallising in white needles, m. p. 136—138°. The *acetyl* derivative of trimethoxytriphenylcarbinol, $C_{19}H_{12}(OMe)_3{\cdot}OAc$, prepared by recrystallisation of the white product from methyl alcohol, forms white crystals, m. p. 105—108°. Both acetyl derivatives readily undergo partial hydrolysis, becoming slightly yellow. It is considered that the immediate product of the acetylation is probably the diacetyl derivative, $C_{19}H_{12}(OMe)_2(OAc)_2$. G. Y.

Relative Stability of Cyclic Polycarbon Groups. LOUIS HENRY (*Compt. rend.*, 1908, **147**, 557—561).—In an earlier paper (Abstr., 1907, i, 374), the author has shown that, under the action of suitable reagents, the tertiary alcohol, dimethyl*iso*propylcarbinol,

$$CHMe_2{\cdot}CMe_2{\cdot}OH,$$

loses H_2O, and the corresponding bromide loses HBr, to form the isomeric ethylenic hydrocarbons, $CMe_2{:}CMe_2$ and $CHMe_2{\cdot}CMe{:}CH_2$, in the proportions of 3 : 1. The investigation has been extended to *cyclo*propyldimethylcarbinol,  $OH{\cdot}CMe_2{\cdot}CH{<}\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array}$, and the results show that the cyclic group,  $-CH{<}\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array}$, is much more stable than the *iso*propyl group, $-CHMe_2$; thus, when *cyclo*propyldimethylcarbinol is treated with acetic anhydride, or its bromide is heated with potassium acetate, the acetate,  $OAc{\cdot}CMe_2{\cdot}CH{<}\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array}$, b. p. 159—160°, is formed; the ethylenic hydrocarbon, α-*cyclopropylpropylene*, b. p. 77°,



$$CH_2{:}CMe{\cdot}CH{<}\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array},$$

is only formed when the alcohol is heated with phosphoric oxide, or the bromide heated at 170° with powdered potassium hydroxide.

M. A. W.

Sodium-alkyl Compounds and Syntheses made Therewith. PAUL SCHORIGIN (*Ber.*, 1908, **41**, 2717—2723).—The author has investigated the action of a mixture of sodium and mercury dialkyls (which probably contains the corresponding sodium dialkyl; compare Buckton, *Annalen*, 1859, **112**, 320) on carbon dioxide, ketones, aldehydes, and esters. The reactions, which confirm the author's assumption that sodium alkyls are formed in syntheses by means of sodium and alkyl halides (this vol., i, 866), are as follows:

$$HgR_2 + 2Na = Hg + 2NaR;$$
$$NaR + R'{\cdot}CO{\cdot}R'' = RR'R''C{\cdot}ONa \longrightarrow RR'R''C{\cdot}OH;$$
$$2NaR + R'{\cdot}CO_2R'' = NaOR'' + RR'R''C{\cdot}ONa \longrightarrow RR'R''C{\cdot}OH;$$
$$NaR + R'{\cdot}COH = RR'CH{\cdot}ONa \longrightarrow RR'CH{\cdot}OH;$$
$$NaR + CO_2 = R{\cdot}CO_2Na \longrightarrow R{\cdot}CO_2H.$$

When an ethereal solution of mercury diethyl and benzophenone is added to ether and sodium, a stream of nitrogen or hydrogen being led through the mixture, a vigorous reaction occurs, with the production of diphenylethylcarbinol in a 40% yield. The αα-diphenylpropylene obtained from this has m. p. 48·5° (Masson, Abstr., 1903, i, 28, gives 51°; the author states that Masson gives 6°, but this is the m. p. ascribed by the latter to diphenylethylene. Klages, Abstr., 1902, i, 668, gives 52°, as do also Hell and Bauer, Abstr., 1904, i, 241). Sodium, mercury diethyl, and methyl benzoate give a 24% yield of phenyldiethylcarbinol, D_4^0 0·9986, D_4^{19} 0·9836, b. p. 109°/15 mm. (Kling, Abstr., 1904, i, 2, gives 125—127°/10 mm.; Grignard, Abstr., 1904, i, 214, gives 101—102°/11 mm.; Klages, Abstr., 1904, i, 28, gives 107—109°/14 mm., and 223—224° under atmospheric pressure).

By the interaction of sodium, mercury diethyl and benzaldehyde, phenylethylcarbinol is produced in a 15% yield, b. p. 108—109°/17 mm.; the density varies from D_4^0 1·017 to 1·020, probably owing to the presence of benzyl alcohol (Wagner, *J. Russ. Phys. Chem. Soc.*, 1884, **16**, 322, gives b. p. 212°, D_0^0 1·016; Errara, Abstr., 1887, 35, gives b. p. 215—217°). A specimen prepared from magnesium ethyl iodide and benzaldehyde had b. p. 108·5°/17 mm., and D_4^0 1·012—1·015. The identity of both preparations was proved by oxidising them to propiophenone, which yielded an identical semicarbazone, m. p. 175° (corr.) (Blaise, Abstr., 1902, i, 164, gives 182°).

By passing a current of carbon dioxide into a mixture of sodium and mercury diethyl in ethereal solution, propionic acid is formed; when mercury dimethyl is used, acetic acid is produced, and by employing mercury di*iso*amyl, *iso*hexoic acid results. J. C. C.

Lupeol. N. H. Cohen (*Arch. Pharm.*, 1908, **246**, 520—522).—It is pointed out that the data recorded by Klobb (Abstr., 1903, i, 165) for anthesterol and its derivatives are in close agreement with those observed for lupeol and the corresponding derivatives of this (Likiernik, Abstr., 1891, i, 551, 1446; Romburgh, 1904, i, 905, and Cohen, 1907, i, 211), and that, consequently, anthesterol may be lupeol.

The same considerations applied to the phytosterol acetate obtained by Marino Zuco (Abstr., 1890, i, 757) from Dalmatian insect flowers, led to the supposition that this might be a mixture of acetates of amyrin and lupeol, but experiments made by the author, whilst giving slightly higher melting points for the various derivatives than those recorded by Marino Zuco, show that the substance contains neither lupeol nor amyrin. T. A. H.

Liquid Crystals of Ergosteryl Esters. Paul Gaubert (*Compt. Rend.*, 1908, **147**, 498—500).—A series of esters prepared from Tanret's ergosterol and fongisterol (this vol., i, 637) has been examined with a view to ascertaining whether, like the esters of the closely-allied cholesterols, they yield liquid crystals (Lehmann, Abstr., 1906, i, 952, and Gaubert, 1907, ii, 939).

Ergosteryl esters present a liquid, anisotropic phase, but this is very difficult to observe in the cases of the acetate and propionate. The crystalline liquids are more viscous than those of the corresponding cholesteryl esters. Ergosterol, cholesterol, and fongisterol, when fused with orcinol, each yield a new compound presenting a liquid, crystal phase. Both ergosterol and fongisterol, when allowed to solidify on a glass slip under a cover glass, do not form spherolites with helical scrolls; this serves to distinguish them from cholesterol and phytosterol. T. A. H.

Double Linkings in Phytosterol and Cholesterol. Ettore Molinari and P. Fenaroli (*Ber.*, 1908, **41**, 2785—2788).—Windaus' supposition, that phytosterol contains two double linkings and cholesterol one (Abstr., 1907, i, 921), is not supported by Willstätter and Mayer (this vol., i, 636) or Langheld (*ibid.*, i, 316), whose results indicate the presence of two double linkings in cholesterol. The authors have therefore examined the behaviour of phytosterol from Calabar beans and nut oil, of cholesterol, and of bombycesterol in chloroform towards ozonised air; in each case an ozonide, $C_{27}H_{46}O_7$, is obtained, the ozone number proving the presence of two double linkings. *Phytosterol ozonide* is a white, crystalline substance, which decomposes at about 100°. The ozone number of ozonides which do not decompose at 50—60° can be determined in two to three hours by saturating the unsaturated compound in a volatile solvent with ozonised air and evaporating the solution to constant weight in a vacuum at 60° on the water-bath.

The authors regard the ozone number as the best indication of the number of true double linkings in an organic compound.

C. S.

Phytosterol from Cotton-seed Oil. A. Heiduschka and H. W. Gloth (*Pharm. Zentr.-h.*, 1908, **49**, 836—837).—The phytosterol of cotton-seed oil, prepared by saponifying the latter and extracting a solution of the soap in water with ether, when acetylated and then brominated as described by Windaus and Hauth (Abstr., 1907, i, 129, 921) does not, like stigmasterol (*loc. cit.*), deposit a crystalline acetate tetrabromide, but only a small quantity of an amorphous *dibromo-acetate* (m. p. 127°, approx.). The substance remaining in solution in the mother liquor is also a *dibromo*-derivative, $C_{29}H_{48}O_2Br_2$, and can be crystallised from alcohol. On treatment with zinc dust and sodium amalgam, it yields the corresponding acetate, and this, on hydrolysis, gives an alcohol, having m. p. 136°, identical with that of the phytosterol started with, so that the latter may be regarded as a single substance. T. A. H.

Phytosterols from Balata. N. H. Cohen (*Arch. Pharm.*, 1908, **246**, 510—514).—A continuation of work on the crystalline constituents of the portion of balata soluble in alcohol (Abstr., 1907, i, 715; compare Tschirch and Schereschewski, Abstr., 1905, i, 713). After the removal of β-amyrin acetate, the residue by crystallisation from alcohol yields two impure products, which can be separated into the same two constituents by the use of (1) mechanical means, followed by (2) fractional crystallisation. The first substance, identical with the β-balalban of Tschirch and Schereschewski (*loc. cit.*), $C_{31}H_{50}O_2$ or $C_{32}H_{52}O_2$, m. p. 111—112°, $[\alpha]_D$ +57° in chloroform, crystallises in colourless leaflets, and, on hydrolysis, furnishes an acid, having the reactions of formic acid, and a crystalline alcohol, m. p. 115—116°. The latter yields an *acetate*, m. p. 107—107·5° (which does not depress the m. p. of the original ester, so that the latter may be the acetate, not the formate), and a *benzoate*, m. p. 120—122·5°, crystallising from alcohol in lustrous leaflets.

The third *constituent*, m. p. 208—210°, crystallises in lustrous leaflets, and, on hydrolysis, yields lupeol (compare Abstr., 1907, i,

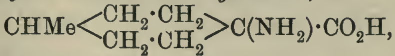
211) and an acid, having the odour of butyric acid, but the silver salt of which contains silver equivalent to that of silver acetate. *Lupeol butyrate*, m. p. 194—195°, crystallises in small, glancing leaflets, and depresses the melting point of the original ester when mixed with it. Lupeol acetate, m. p. 215°, does not depress the melting point of the original ester when mixed with it, but as the synthetic ester crystallises in needles and the natural one in leaflets, it is suggested that the latter may be the acetate of an isomeride of lupeol, which is converted into lupeol in the process of hydrolysis, or again, the difference in crystalline form may be due to the presence of an impurity in the natural ester, as prepared from balata. T. A. H.

Phytosterols from South African "Rubber." N. H. Cohen (*Arch. Pharm.*, 1908, **246**, 515—520).—The coagulated latex from a South African *Euphorbia*, which contained 70·0% of resin and only 5·5% of a caoutchouc-like substance, has been systematically examined with a view to the identification of the resin-alcohols it contains.

An extract of the product in boiling alcohol deposits, first, β-amyrin acetate, and eventually a second *substance*, $C_{30}H_{50}O$, m. p. 112—116°, $[\alpha]_D$ + 8·75° in chloroform, which crystallises from cold alcohol in thin, lustrous, colourless leaflets, and is not affected by boiling with potassium hydroxide in alcohol. With acetic anhydride, it furnishes an *acetate*, m. p. 117—122°, $[\alpha]_D$ + 25° in chloroform, but when heated with benzoyl chloride it yields two crystalline products, m. p. 146—152° and m. p. 159—164°, and these, on hydrolysis, furnish substances of m. p. 110·5—111° and 115—117·5° respectively, indicating possibly that the parent alcohol, m. p. 110°, may have been a mixture of two substances.

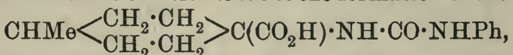
For the detection of lupeol (compare Abstr., 1907, i, 211), the portion of the coagulated latex soluble in alcohol was treated with potassium hydroxide in alcohol, and the neutral hydrolytic product benzoylated. No lupeol benzoate was found, but, in addition to amyrin benzoate, a second *substance*, $C_{31}H_{44}O$ or $C_{33}H_{48}O_2$, m. p. 193—195°, $[\alpha]_D$ + 75° in chloroform, crystallising from acetone in glancing needles, was obtained. This, on hydrolysis by alkalis in alcohol, gave a *product*, $C_{24}H_{40}O,H_2O$ or $C_{26}H_{44}O,H_2O$, $[\alpha]_D$ + 58·6°, which crystallises in needles from acetone diluted with water, and in some respects resembles Schulze's *iso*cholesterol (Abstr., 1898, i, 463), but, whilst the latter, according to Schulze, gives an amorphous acetate, the phytosterol from this Euphorbia latex yields a crystalline acetate, $C_{26}H_{42}O_2$ or $C_{28}H_{46}O_2$, m. p. 134—135°. T. A. H.

Hydrocyclic α-Amino-acids. Aladar Skita and R. Levi (*Ber.*, 1908, **41**, 2925—2937).—The comparison of aliphatic and alicyclic α-amino-acids is not without interest, since recent researches (Zelinsky and Gutt, this vol., i, 638; Merling, *ibid.*, i, 653) have shown not unimportant differences in the behaviour of aliphatic and alicyclic carboxylic acids. Whilst the esters of *cis*-hydrocyclic δ-amino-acids yield unimolecular anhydrides by treatment with sodium ethoxide (Skita, Abstr., 1907, i, 1040), a similar behaviour of hydrocyclic α-amino-acids is impossible, since the amino- and the carboxyl groups, being attached to the same carbon atom, must always have the *trans*-configuration. The esters of such amino-acids ought to yield bimolecular anhydrides, cyclic 2:5-diketopiperazines, which should hydrolyse to cyclic dipeptides. Such behaviour has been observed in the cases of 4-*amino*-1-*methyl*cyclo*hexane*-4-*carboxylic acid*,



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C(NH_2)\cdot CO_2H},$$

and 2-*amino*-1-*methyl*cyclo*hexane*-2-*carboxylic acid*. The first acid is obtained by treating 1-methyl*cyclo*hexan-4-one (Wallach, Abstr., 1906, i, 514) with concentrated aqueous potassium cyanide and ammonium chloride, and hydrolysing the resulting amino-nitrile (*hydrochloride*, $C_8H_{14}N_2,HCl$, m. p. 191°, decomp.) by ten hours' boiling with concentrated hydrochloric acid; it has m. p. above 300°, forms a blue *copper* salt, $(C_8H_{14}O_2N)_2Cu,H_2O$, has a neutral reaction, and is tasteless. Nitrous acid converts it into the corresponding *hydroxy-acid*, $C_8H_{14}O_3$, m. p. 115°, whilst the reaction between equal molecular quantities of the acid and phenylcarbimide in alkaline solution leads to the formation of the *phenylcarbamido-acid*,



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C(CO_2H)\cdot NH\cdot CO\cdot NHPh},$$

m. p. 190°, which, warmed with 25% hydrochloric acid, yields the corresponding cyclic *hydantoin*, $C_{15}H_{18}O_2N_2$, m. p. 184°.

2-Amino-1-methyl*cyclo*hexane-2-carboxylic acid is best obtained by heating 1-methyl*cyclo*hexan-2-one, dissolved in light petroleum, for two hours at 60° with potassium cyanide, ammonium chloride, and a little water, and hydrolysing the resulting amino-nitrile (the *hydrochloride*, $C_8H_{14}N_2,HCl$, decomposes at 182°) by ten hours' heating with concentrated hydrochloric at 100° under pressure; 1-methyl*cyclo*hexan-2-one is obtained as a by-product. The acid has a sweet taste, and melts above 300°; the *naphthylcarbamido-acid*, $C_{19}H_{22}O_3N_2$, has m. p. 180° (decomp.). In this acid, steric hindrance caused by the neighbouring methyl group (compare also Skita, *loc. cit.*) is observed, not only during the hydrolysis of the preceding amino-nitrile, but also in the esterification of the acid and in the hydrolysis of the resulting ester. Whilst 4-amino-1-methyl*cyclo*hexane-4-carboxylic acid is readily esterified by alcoholic hydrogen chloride, the isomeric acid must be saturated in alcoholic solution with hydrogen chloride and heated for ten hours at 100° under pressure. The esters are very reactive liquids, with a basic odour and an alkaline reaction.

Ethyl 4-*amino*-1-*methyl*cyclo*hexane*-4-*carboxylate*, $C_{10}H_{19}O_2N$, b. p. 103—105°/11 mm., D^{20} 0·928, is easily hydrolysed by boiling water, produces local anæsthesia like the esters of δ-amino-acids, and forms a *picrate*, $C_{16}H_{22}O_9N_4$, m. p. 185°, and a *phenylthiocarbamide*, $C_{17}H_{24}O_2N_2S$, m. p. 205—206°. By treating the ester in chloroform with *d*-alanyl chloride and hydrolysing the resulting ester, a mixed aliphatic, alicyclic *dipeptide* is obtained, $C_{11}H_{20}O_3N_2$, which has m. p. above 300°, and $[\alpha]_D^{20}$ 22·33° in 21% hydrochloric acid. *Ethyl* 2-*amino*-1-*methyl*cyclo*hexane*-2-*carboxylate*, b. p. 99—100°/12 mm., forms a *phenylthiocarbamide*, m. p. 198—199°, and requires heating with sodium hydroxide for hydrolysis to occur.

The esters of both acids are converted by twenty to twenty-four hours' heating at 200° into cyclic *derivatives* of 2:5-diketopiperazine,

$C_7H_{12}<\begin{matrix}CO\cdot NH\\NH\cdot CO\end{matrix}>C_7H_{12}$, which melt above 300°; the one derived from 4-amino-1-methyl*cyclo*hexane-4-carboxylic acid can be partly hydrolysed by concentrated hydrobromic acid at 100° under pressure, yielding a cyclic *dipeptide*, $CO_2H\cdot C_7H_{12}\cdot NH\cdot CO\cdot C_7H_{12}\cdot NH_2$, which is isolated as the reddish-violet *copper* salt, $(C_{16}H_{27}O_3N_2)_2Cu$.

C. S.

New Synthesis of Aromatic Carboxylic Acids from the Hydrocarbons. PAUL SCHORIGIN (*Ber.*, 1908, 41, 2723—2728).—The author has shown that when carbon dioxide acts on a mixture of sodium and mercury alkyl in ethereal solution, the corresponding aliphatic acid is produced (this vol., i, 882). When dry benzene is used instead of ether in this reaction, in addition to the aliphatic acid, benzoic acid is formed in considerable amount. The reaction is due, as in the previous case, to the intermediate formation of sodium alkyl, for by the interaction of carbon dioxide, sodium, and benzene, or of carbon dioxide, mercury diethyl, and benzene, benzoic acid is not obtained. In this reaction the mercury diethyl can be replaced by zinc diethyl, but the yields are smaller: $C_6H_6 + C_2H_5Na = C_6H_5Na + C_2H_6$; $C_6H_5Na + CO_2 = C_6H_5\cdot CO_2Na$.

The reaction proceeds also in the case of other aromatic hydrocarbons, but the carboxyl group enters the side-chain; thus toluene gives phenylacetic acid, *m*-xylene gives *m*-tolylacetic acid, and ethylbenzene yields α-phenylpropionic acid. When zinc diethyl is used instead of mercury diethyl, toluene gives *p*-toluic acid in addition to phenylacetic acid.

In addition to these acids, neutral by-products are sometimes formed; thus benzene yields a small amount of triphenylmethane mixed with triphenylcarbinol, produced according to the scheme:

$$CO_2 + 3NaPh = Na_2O + CPh_3\cdot ONa$$
$$CPh_3\cdot ONa \longrightarrow CPh_3\cdot OH \longrightarrow CHPh_3,$$

and ethylbenzene gives a *hydrocarbon*, $C_{16}H_{18}$, which is a colourless liquid with a weak, sweetish, aromatic odour, b. p. 161—163°/13 mm., D_4^0 0·9858, D_4^{25} 0·9685, and is very stable towards oxidising agents. Negative results were obtained on applying the reaction to *cyclo*hexane and di*iso*amyl.

J. C. C.

Derivatives of 3 : 5-Di-iodo-*l*-tyrosine. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Ber.*, 1908, 41, 2852—2857. Compare this vol., i, 420).—Acid chlorides containing iodine, when coupled with amino-acids, yield compounds which crystallise better than the corresponding bromine derivatives. Their use is attended, however, with the disadvantage that they cause racemisation; thus, *d*-bromopropionic acid and potassium iodide react to give optically inactive iodopropionic acid.

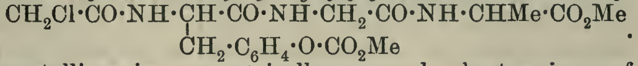
Iodoacetic acid is obtained in colourless plates, m. p. 83°, by the interaction of potassium iodide and monochloroacetic acid. *Iodoacetyl chloride*, $CH_2I\cdot CO\cdot Cl$, prepared by warming the acid with thionyl chloride, is a heavy oil, b. p. 49—52°/15 mm., D^{25} 2·25. At the same time, *iodoacetic anhydride* is formed in transparent, colourless crystals, m. p. 46°.

Ethyl iodoacetyltyrosine forms rhombic, colourless, crystalline plates, m. p. 120° (corr.). By the action of iodine and sodium hydroxide, it is converted into 3 : 5-*di-iodo-α-iodoacetyl*-l-*tyrosine*,

$$OH\cdot C_6H_2I_2\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH_2I,$$

which crystallises in colourless, prismatic needles, becoming brown at 190° (corr.), and m. p. 209° (corr., decomp.). *dl*-α-Iodopropionic acid is conveniently prepared in colourless crystals, m. p. 45·5° (corr.), by the interaction of bromopropionic acid with potassium iodide. dl-*α-Iodopropionyl chloride*, $CH_3\cdot CH_2I\cdot COCl$, is a faintly-brown, pungent-smelling oil, b. p. 51—53°/13 mm., D^{25} 1·989. *Ethyl* dl-*α-iodopropionyl*-l-*tyrosine* crystallises in colourless plates, m. p. 126°, to a colourless oil. dl-3 : 5-*Di-iodo-α-iodopropionyl*-l-*tyrosine* crystallises in fine needles, m. p. 210·5° (corr., decomp.). dl-3 : 5-*Di-iodoalanyl*-l-*tyrosine*, obtained by the action of ammonia on the foregoing, has m. p. 217—219°, $[\alpha]_D^{20}$ +47·23°. E. F. A.

The Synthesis of Polypeptides. XXV. Derivatives of Tyrosine and of Aminoacetal. Emil Fischer (*Ber.*, 1908, 41, 2860—2875).—In part already published (this vol., i, 544). A tetrapeptide containing tyrosine was obtained by the following method. The *hydrochloride* of *glycyl*-d-*alanine methyl ester*, prepared by the action of gaseous hydrogen chloride and dry methyl alcohol on the dipeptide, forms thin, colourless, silky, glistening prisms, m. p. 160—162° (corr.). This salt is decomposed by a little less than the calculated quantity of sodium methoxide, and is immediately used for further synthesis, as it easily passes over into glycine-*d*-alanine anhydride. Coupled with chloroacetyltyrosyl chloride methyl carbonate, it yields *methyl chloroacetyl-tyrosyl-glycyl*-d-*alanine ester methyl carbonate*,



$$CH_2Cl\cdot CO\cdot NH\cdot \underset{CH_2\cdot C_6H_4\cdot O\cdot CO_2Me}{\underset{|}{CH}}\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2Me.$$

This ester crystallises in concentrically-arranged, short prisms of a faint yellow colour, which sinter at 200°, m. p. 208° (corr.), to a yellow liquid. On hydrolysis, the tetrapeptide, *glycyl-tyrosyl-glycyl*-d-*alanine*, is formed. This is an amorphous, faintly yellow powder, which, quickly heated, colours at 180—190° and decomposes at 225° (corr.). It is precipitated like the albumoses by saturated ammonium sulphate in concentrated solution, but not in dilute solution. It is probably a mixture of stereoisomerides.

Formyl-l-*tyrosine methyl carbonate*,

$$CHO\cdot NH\cdot CH(CH_2\cdot C_6H_4\cdot O\cdot CO_2Me)\cdot CO_2H,$$

crystallises from water in glistening, large, thin plates, which sinter at 142°, m. p. 147° (corr.), $[\alpha]_D^{20}$ +66·7°. *Formyl*-l-*tyrosine ethyl carbonate* forms centimetre-long, thin, silky, glistening needles, m. p. 177—179° (corr., decomp.), after sintering at 173°. E. F. A.

Synthesis of Polypeptides. XXVIII. Derivatives of Glycine, *d*-Alanine, *l*-Leucine, and *l*-Tyrosine. Emil Abderhalden and Alfred Hirszowski (*Ber.*, 1908, 41, 2840—2851).—The presence of *l*-tyrosine in polypeptides may possibly give them properties similar to those of the albumoses, but, in addition, the position of the tyrosine in the molecule must be defined. The polypeptide isolated by Fischer and Abderhalden (Abstr., 1907, i, 737, 990) from silk consists of two molecules of glycine, one of *d*-alanine, and one of *l*-tyrosine; on partial hydrolysis, it yields glycyl-*d*-alanine anhydride and glycyl-*l*-tyrosine anhydride. Of the eight possible stereoisomeric polypeptides of this composition, but one has been prepared synthetically; this, however, is not precipitated by ammonium sulphate. The polypeptides now described containing tyrosine are likewise not precipitated by ammonium sulphate.

Ethyl *l*-tyrosine and *d*-*α*-bromopropionyl chloride were coupled by Fischer's method to *ethyl* d-*α-bromopropionyl*-l-*tyrosine*, which crystallises in bunches of long plates, m. p. 133·5—134·5° (corr.). On hydrolysis, it is converted into d-*α-bromopropionyl*-l-*tyrosine*, which forms crystalline plates pointed at both ends, m. p. 165° (corr.), and, when treated with ammonia, forms d-*alanyl*-l-*tyrosine*,

$$NH_2\cdot CHMe\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH.$$

The dipeptide crystallises in large, hexagonal plates, m. p. (frothing) 202° (decomp. at 285°, corr.), and has $[\alpha]_D^{20}$ +43·14°. It is rapidly hydrolysed by the pancreas extract of the dog.

d-3:5-*Di-iodo-α-bromopropionyl*-l-*tyrosine*,

$$CHMeBr\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_2I_2\cdot OH,$$

prepared by the action of iodine in chloroform on bromopropionyltyrosine ester dissolved in sodium hydroxide, crystallises in rosettes of long, thin needles, m. p. 217° (corr., decomp.). By the action of ammonia, it is converted into d-*alanyl*-3:5-*di-iodo*-l-*tyrosine*,

$$NH_2\cdot CHMe\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_2I_2\cdot OH,$$

which, on heating, becomes yellow at 188°, brown at 205°, and has m. p. 231° (corr., decomp.).

d-*α-Bromo*iso*hexoyl*-l-*tyrosine* is obtained as an amorphous solid, m. p. 141·5° (corr.), by the interaction of ethyl tyrosine and *d*-*α*-bromo*iso*hexoyl chloride. l-*Leucyl*-l-*tyrosine*, as prepared by the action of aqueous ammonia on the foregoing, is amorphous. It has m. p. 269° (corr., decomp.), $[\alpha]_D^{20}$ +10·37°, and is hydrolysed by pancreas extract.

Chloroacetyl-d-*alanyl*-l-*tyrosine*, prepared by coupling chloroacetyl chloride with *d*-alanyl-*l*-tyrosine, is amorphous, sinters at 97°, m. p. 108°, and decomp. 236°. *Glycyl*-d-*alanyl*-l-*tyrosine*,

$$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH,$$

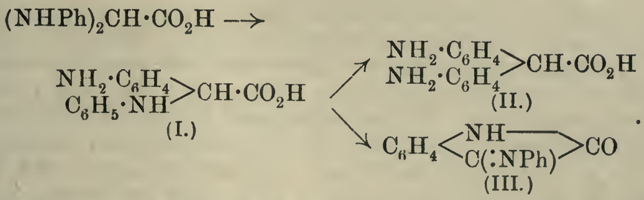
is also amorphous; it becomes yellow at 193°, m. p. 208° (corr., decomp.), and has $[\alpha]_D^{20}$ −4·83°. It gives an amorphous precipitate with phosphotungstic acid, but only a slight clouding with ammonium sulphate.

d-*α-Bromopropionyldiglycylglycine*, prepared from diglycylglycine and *d*-bromopropionyl chloride, crystallises in bunches of slender needles, m. p. 189·5°. d-*Alanyldiglycylglycine*,

$$NH_2\cdot CHMe\cdot CO\cdot [NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2H,$$

crystallises in minute needles, m. p. 253·7° (corr., decomp.), $[\alpha]_D^{20}$ +27°, and is rapidly attacked by pancreas juice. E. F. A.

Action of Dichloroacetic Acid on Aniline and its Homologues. II. IWAN OSTROMISSLENSKY (*Ber.*, 1908, 41, 3019—3028. Compare this vol., i, 82).—In the direct action of dichloroacetic acid with an excess of an arylamine, the various stages appear to be those represented by the following formulæ :



$$(NHPh)_2CH\cdot CO_2H \longrightarrow \underset{\text{(I.)}}{\begin{matrix}NH_2\cdot C_6H_4\\ C_6H_5\cdot NH\end{matrix}>CH\cdot CO_2H} \begin{matrix}\nearrow \underset{\text{(II.)}}{\begin{matrix}NH_2\cdot C_6H_4\\ NH_2\cdot C_6H_4\end{matrix}>CH\cdot CO_2H} \\ \searrow \underset{\text{(III.)}}{C_6H_4<\begin{matrix}NH\text{——}\\ C(:NPh)\end{matrix}>CO}\end{matrix}$$

The dianilinoacetic acid is unstable, and undergoes the Hofmann rearrangement either singly or in duplicate. In the former case, the acid formed (I) loses water and yields imesatin (III), and in the latter case the product is 4 : 4′-diaminodiphenylacetic acid (II). The dianilinoacetic acid cannot be isolated from the products of the reaction on account of its instability in the presence of an excess of the amine ; it may, however, be obtained by the action of aniline on glyoxylic acid.

4 : 4′-*Diaminodiphenylacetic acid* crystallises from alcohol, in which imesatin is readily soluble, as soft, dark-coloured flakes, which, when powdered, have a pale canary-yellow colour. It melts at 73—74° to a dark brown oil, resolidifies, and then has m. p. 233—234° (decomp.). The crystals contain 1 mol. of alcohol, which they lose when heated for fifteen hours at 90°. The product is then dark yellow, and decomposes at 215°. The presence of amino-groups is shown by the readiness with which it can yield azo-dyes, and its constitution follows (*a*) from the fact that, when heated with dilute hydrochloric acid, it loses carbon dioxide and yields 4 : 4′-diaminodiphenylmethane, and (*b*) from the presence of four active hydrogen atoms (compare Zerewitinoff, this vol., i, 593).

A second modification (β) of the diamino-acid is obtained when ether is added to its alcoholic solution. It is excessively unstable, and, when brought into contact with the air, yields a dark-coloured oil, which is transformed into the original modification (α) when kept over sulphuric acid. J. J. S.

Action of Glyoxylic Acid and of Diacetylglyoxylic Acid on Aniline and its Homologues. IWAN OSTROMISSLENSKY (*Ber.*, 1908, 41, 3029—3034).—The product described by Böttinger (Abstr., 1879, 51) as the aniline salt of anilglyoxylic acid is shown to be the unstable dianilinoacetic acid. This follows (*a*) from the readiness with which aniline is eliminated, yielding anilglyoxylic acid, and (*b*) from the readiness with which it is transformed into 4 : 4′-diaminodiphenylacetic acid.

Di-p-*toluidinoacetic acid*, obtained from glyoxylic acid and *p*-toluidine, forms hard, colourless crystals, m. p. about 96°, becoming yellowish-red when kept. *Ethyl di*-p-*toluidinoacetate*, $CH(NH\cdot C_6H_4Me)_2\cdot CO_2Et$, obtained from the base and ethyl glyoxylate, forms colourless crystals. m. p. 170°, and readily yields *p*-tolyl-*p*-methylimesatin when warmed with mineral acids. J. J. S.

The Three Chloroacetyl-benzyl Cyanides [Chloroacetylphenylacetonitriles] and Their Derivatives. Franz Kunckell [and F. Flos] (*Ber.*, 1908, **41**, 3046—3050. Compare Abstr., 1906, i, 848).—Chloroacetyl chloride reacts much more vigorously with phenylacetonitrile in the presence of aluminium chloride than with acetyl chloride. When the condensation is carried out in the presence of carbon disulphide, the product consists of a mixture of o-, m-, and p-*chloroacetylphenylacetonitriles.* The para-compound solidifies when the crude product is kept, and is freed from the two isomerides by pressing on porous plate. It crystallises from a mixture of benzene and light petroleum in colourless needles, m. p. 93°. The ortho-compound is obtained as a solid when the oily residue from the para-compound is distilled under diminished pressure and kept for some days, or a large yield can be obtained from the acid liquor formed when the initial condensation product is added to water. It crystallises from water in glistening, snow-white needles, m. p. 47°. m-*Chloroacetylphenylacetonitrile* is an oil, b. p. 210—215°/25 mm. Each of the three compounds can be oxidised by alkaline hydrogen peroxide to the corresponding phthalic acid.

p-*Chloroacetylphenylacetic acid*, $CH_2Cl\cdot CO\cdot C_6H_4\cdot CH_2\cdot CO_2H$, prepared by hydrolysing the nitrile with fuming hydrochloric acid at 120—130°, forms yellow needles, m. p. 130°. Fuming nitric acid converts the nitrile into 3-*nitro-4-chloroacetylphenylacetic acid*,

$$CH_2Cl\cdot CO\cdot C_6H_3(NO_2)\cdot CH_2\cdot CO_2H,$$

which crystallises from water in yellow, glistening needles, m. p. 149°. Its solutions in alkalis have a deep blue colour, but turn yellow when boiled. When the nitrile is heated for two hours at 70—100° with fuming nitric acid, the product is *glyoxylnitrophenylacetic acid*,

$$CO_2H\cdot CO\cdot C_6H_3(NO_2)\cdot CH_2\cdot CO_2H,$$

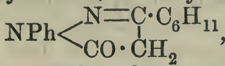
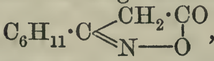
which crystallises from ether in yellow needles, m. p. 214°. Its solutions in alkali hydroxides are blue, but in ammonia, yellow.

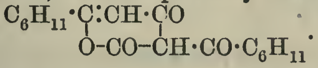
J. J. S.

A Dextrorotatory Resin Acid. W. Schkateloff (*Chem. Zentr.*, 1908, ii, 807; from *Mon. Sci.*, 1908, **22**, [ii], 548).—If a solution of crude β-sylvic acid, saturated with sulphur dioxide, is allowed to crystallise, the mother liquor will, after a time, deposit *d-sylvic acid* as a crystalline powder. When recrystallised from ether, it is obtained in rectangular plates, soluble in alkaline solutions, $[\alpha]_D + 78°$.

J. V. E.

Esters of Hexahydrobenzoylacetic Acid. André Wahl and A. Meyer (*Bull. Soc. chim.*, 1908, [iv], **3**, 957—963).—Most of the results recorded have been published already (Abstr., 1907, i, 765), but detailed accounts of the methods of preparation and new constants for the various substances described are now given.

Ethyl hexahydrobenzoylacetate, $C_6H_{11}\cdot CO\cdot CH_2\cdot CO_2Et$, b. p. 145—147°/19 mm., D^0 1·039, D^{18} 1·025 (compare Zelinsky and Schwedoff, Abstr., 1907, i, 704), is a colourless liquid, insoluble in water, soluble in most organic solvents, and gives a violet coloration with ferric chloride; the copper salt, m. p. 120°, separates from a mixture of ether and light petroleum in green leaflets. The methyl ester, b. p. 138°/20 mm., yields a similar copper salt, m. p. 137—138°. With phenylhydrazine, the ethyl ester furnishes 1-*phenyl*-3-cyclo*hexyl*-5-*pyrazolone*,  $\mathrm{NPh}<\begin{matrix}\mathrm{N{=}C\cdot C_6H_{11}}\\ \mathrm{CO\cdot CH_2}\end{matrix}$, m. p. 126°, which crystallises in colourless spangles from boiling alcohol. With hydroxylamine, 3-cyclo*hexyl*iso*oxazolone*,  $\mathrm{C_6H_{11}\cdot C}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{N{-}O}\end{matrix}$, m. p. 42°, is produced. This crystallises in needles, several centimetres in length, and is readily soluble in alcohol or ether, less so in water or light petroleum.

The residues obtained in the preparation of ethyl hexahydrobenzoylacetate deposit eventually slender, silky, colourless needles of a *substance*, m. p. 90—91°, which is probably 3-*hexahydrobenzoyl*-6-cyclo*hexyl*-2 : 4-*pyronone*,  $\begin{matrix}\mathrm{C_6H_{11}\cdot C{:}CH\cdot CO}\\ \mathrm{O{-}CO{-}CH\cdot CO\cdot C_6H_{11}}\end{matrix}$. T. A. H.

Salicylic Acid-Iron Reaction. Karl Hopfgartner (*Monatsh.* 1908, **29**, 689—712).—An account is given of the views of various authors as to the cause of the violet coloration produced by adding salicylic acid to solutions of ferric salts. A new study of the reaction has led to the isolation of two *ferrisalicylic acids* :

(I) $\mathrm{OH\cdot Fe(C_7H_5O_3)_2,H_2O}$ and (II) $\mathrm{OH\cdot Fe_4O(C_7H_5O_3)_9}$.

The compound (I), which is obtained when slightly less than 3 mols. of sodium salicylate are added to 1 mol. of ferric chloride in moderately concentrated aqueous solution at the ordinary temperature, or on prolonged shaking of ferric hydroxide with salicylic acid and water, forms blackish-violet, microscopic needles, is stable at 100°, but decomposes at higher temperatures, and dissolves in water or dilute ferric chloride, forming a violet solution ; hence it is to be considered as the cause of the violet coloration of the salicylic acid-iron reaction. The compound (II), formed by the action of sodium salicylate on ferric chloride, in hot concentrated solution, or by heating the acid (I) with salicylic acid at 155—160°, crystallises from ether-alcohol in scarlet, microscopic prisms containing ether, becomes blackish-brown when dried at 100°, decomposes at higher temperatures, and is converted into the acid (I) on prolonged shaking with water, the conversion being accelerated by gentle heating.

Ferric chloride and sodium 5-bromosalicylate form, in the same manner, two *ferribromosalicylic acids*, $\mathrm{OH\cdot Fe(C_7H_4O_3Br)_2,\frac{1}{2}H_2O}$ and $\mathrm{OH\cdot Fe_4O(C_7H_4O_3Br)_9}$; *p*-hydroxybenzoic acid, on the other hand, is found to form only one *ferri*-compound, $\mathrm{OH\cdot Fe(C_7H_5O_3)_2,H_2O}$.

Hantzsch and Desch's ferrisalicylic acid (Abstr., 1902, i, 708), prepared from ferric chloride, sodium acetate, and salicylic acid, is considered to have the constitution $\mathrm{Fe_4(OH)_3(C_7H_5O_3)_9}$, and to be related, therefore, to the ferrisalicylic acid (I). If insufficient salicylic acid is employed in its preparation, a *product*,

$$\mathrm{OH\cdot FeO(C_7H_5O_3)_8\cdot C_2H_3O_2},$$

is obtained.

In agreement with Hantzsch and Desch's view, that in such compounds the ferric atom displaces phenolic hydrogen atoms, it is found that, when heated with alcohol, ferrisalicylic acid (II) forms an *ethyl* ester, $OH\cdot Fe_4O(C_7H_5O_3)_8\cdot C_7H_4O_3Et$ or

$$Fe_4(OH)_3(C_7H_5O_3)_8\cdot C_7H_4O_3Et,$$

which points to the presence of a free carboxyl in the original compound. A similar *ethyl* ester, $OH\cdot Fe_4O(C_7H_4O_3Br)_8\cdot C_7H_3O_3BrEt$, is obtained from the second ferribromosalicylic acid. Moreover, a crystalline *ferri*-compound, $Fe(C_7H_5O_2)_3$, is formed by the action of salicylaldehyde and 10% potassium hydroxide on ferric chloride in concentrated solution. On the other hand, the ferrisalicylic acid (II) is of complex nature, since it does not form silver salicylate with silver nitrate in alcoholic solution, a reaction which takes place directly with sodium salicylate; the salicylic acid in the complex is considered to be "masked" in the same manner as is the sulphuric acid in green chromium sulphate. G. Y.

Methyl-carbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetical Operations. Emil Fischer (*Ber.*, 1908, 41, 2875—2891).—Chlorides of phenolcarboxylic acids cannot be prepared by ordinary methods, as the chlorides of phosphorus attack both carbonyl and hydroxyl, and yield products containing phosphorus. When, however, by means of methyl chlorocarboxylate, the phenol group is first converted into a methyl-carbonato-compound, a normal acid chloride results, which is available for manifold synthetical purposes. On hydrolysis of the new products with cold alkali hydroxide, the original phenolic group is regenerated (compare this vol., i, 544).

p-*Methyl-carbonatobenzoic acid*, $CO_2Me\cdot O\cdot C_6H_4\cdot CO_2H$, is obtained almost quantitatively from *p*-hydroxybenzoic acid and methyl chlorocarbonate. It crystallises in colourless, short needles, m. p. 179° (corr.), and gives no coloration with ferric chloride or with Millon's reagent. p-*Methyl-carbonatobenzoyl chloride*, prepared by the action of phosphorus pentachloride on the above, forms colourless, long needles, m. p. 82—83° (corr.), and distils without decomposition by 10—15 mm.

It combines with glycine ester to *ethyl* p-*methyl-carbonatobenzoylglycine*, $CO_2Me\cdot O\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, which crystallises in needles, m. p. 63° (corr.), and, when hydrolysed with sodium hydroxide, yields p-*hydroxyhippuric acid*, $OH\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$. This separates in colourless, thin, glistening prisms, m. p. 240° (corr.), to a yellow liquid, and subsequently decomposes; it gives a brown coloration with ferric chloride, and is coloured red by Millon's reagent. It is, perhaps, identical with an acid, m. p. 228°, isolated from pathological urine.

3 : 4-*Dimethyl-carbonatobenzoic acid*, $(CO_2Me\cdot O)_2C_6H_3\cdot CO_2H$, is obtained in colourless needles, m. p. 165—166°. 3 : 4-*Dimethyl-carbonatobenzoyl chloride* crystallises in bunches of needles, m. p. 118° (corr.), which sinter 2° or 3° lower.

3 : 4 : 5-*Trimethyl-carbonatobenzoic acid*, $(CO_2Me\cdot O)_3\cdot C_6H_2\cdot CO_2H$, is obtained by the interaction of gallic acid and methyl chlorocarbonate in an atmosphere of hydrogen in a special apparatus. It forms colourless, thin prisms, which sinter about 130°, m. p. 136—141°. It forms a

crystalline, colourless *bromo*-derivative and a soluble *pyridine* salt, which is decomposed by excess of the base and liberates carbon dioxide. It is completely hydrolysed by acids, alkaline hydroxides, or ammonia to gallic acid; the methylcarbonato-group is eliminated as methyl carbamate by ammonia. Cautious partial hydrolysis in an atmosphere of hydrogen yields *hydroxydimethylcarbonatobenzoic acid*, $(CO_2Me\cdot O)_2\cdot C_6H_2(OH)\cdot CO_2H$. This has m. p. 160° (corr.), and gives a dark green coloration with ferric chloride.

3:4:5-*Trimethylcarbonatobenzoic acid* crystallises in colourless, glistening plates, m. p. 96—97° (corr.).

3:4:5-*Trimethylcarbonatobenzoyl chloride* forms long needles, m. p. 86° (corr.) to a clear liquid; it reacts with dimethylaniline and also with aniline, forming in the latter case *trimethylcarbonatobenzoic anilide*, which crystallises in needles pointed at both ends, m. p. 175—176° (corr.) to a clear liquid. p-*Trimethylcarbonatobenzoyloxybenzoic acid*, $(CO_2Me\cdot O)_3\cdot C_6H_2\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, is obtained as an oil, which solidifies to thin prisms aggregated in bunches, m. p. 165° (corr.). On hydrolysis, for which purpose the crude product may be used with advantage, it yields p-*galloyloxybenzoic acid*,

$$C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H.$$

This is obtained as a sandy, crystalline powder, consisting of obliquely cut plates, m. p. 260° (corr., decomp.). It gives similar colorations to gallic acid with ferric chloride or potassium cyanide.

On coupling trimethylcarbonatobenzoyl chloride with hydroxydimethylcarbonatobenzoic acid in alkaline solution, an amorphous mass was obtained, which contained much *pentamethylcarbonatobenzoyloxybenzoic acid*, and, on hydrolysis, yielded what appeared to be a mixture of gallic acid with *digallic acid*,

$$C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(OH)_2\cdot CO_2H\ ;$$

it formed short prisms or needles, m. p. 275—280° (decomp.).

E. F. A.

Nitration. IV. Nitration of *N*-Acyl Compounds of Aniline derived from Certain Polybasic, Aliphatic, and Aromatic Acids. J. Bishop Tingle and F. C. Blanck (*J. Amer. Chem. Soc.*, 1908, 30, 1587—1599. Compare this vol., i, 778).—A study has been made of the nitration of anilides of various di- and tri-basic acids, the experiments being carried out under the same general conditions as those described previously.

Oxanilic acid yields the *p*-nitro-derivative, both on direct nitration and also on nitration in presence of oxalic acid. Oxanilide gives the *m*-nitro-derivative in presence of sulphuric acid, and the *p*-dinitro-derivative in presence of acetic acid. Succinanilic acid yields the *m*-nitro-derivative in presence of sulphuric acid, and the *p*-nitro-derivative in presence of oxalic acid. By direct nitration of succinanil, a mixture of ortho- and para-derivatives is obtained, but in presence of sulphuric or oxalic acid, the *p*-nitro-derivative is formed. On direct nitration, succinanilide yields the *s*-*p*-dinitro-derivative, and tartranilide gives the *p*-nitro-derivative.

Phthalanil, both on direct nitration and in presence of oxalic acid, yields the *p*-nitro-derivative. Citranilide, on direct nitration, gives a trinitro-derivative.

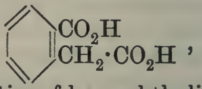
The experiments so far carried out have led to the following generalisations. Direct nitration yields either the para-derivative or a mixture of ortho- and para-derivatives, except in the case of benzanilide, which gives some meta-derivative. Nitration in presence of sulphuric acid gives chiefly, or exclusively, the *m*-nitro-derivative. Oxalic acid does not affect the course of the nitration, and this is probably due to its small solubility in nitric acid.

The possible modes of representing the disubstituted benzenes are discussed, and it is stated that the authors' results are fully and satisfactorily accounted for by Barlow and Pope's formula for benzene (Trans., 1906, **89**, 1697).

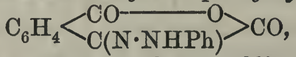
A discussion is also given of the mechanism of substitution, and leads to the conclusion that substitution must be regarded as essentially an additive phenomenon (compare Armstrong, Proc., 1891, **7**, 89). E. G.

Homophthalic Esters, Oxymethylenehomophthalic Esters, and their *iso*Coumarin and *iso*Carbostyril Derivatives. WALTHER DIECKMANN and WILHELM MEISER (*Ber.*, 1908, **41**, 3253—3269).—The structural analogy existing between homophthalic and glutaconic acids:

$$\begin{array}{l} CH\cdot CO_2H \\ \| \\ CH\cdot CH_2\cdot CO_2H \end{array}$$



suggested an investigation into the properties of homophthalic acid with a view to comparing them with those of the other acid. The methylene group, which is very reactive in glutaconic acid (compare Henrich, Abstr., 1902, i, 422), is markedly less reactive in the aromatic derivative. Sodium ethoxide and benzyl bromide are without action on ethyl homophthalate, as is also diazobenzene chloride. With homophthalic anhydride, however, the diazo-salt forms *benzeneazohomophthalic anhydride* [*phthalonic anhydride phenylhydrazone*],



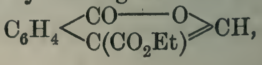
$$C_6H_4{<}\begin{matrix}CO\text{———}O\\C(N\cdot NHPh)\end{matrix}{>}CO,$$

which crystallises from benzene in long, reddish-yellow needles, m. p. 199°. It is hydrolysed by acids or alkalis to 3-phenylphthalazone-1-carboxylic acid. This marked difference between the acid and its anhydride is ascribed to the formation of the ring. Ethyl homophthalate yields naphthalene derivatives on condensation with sodium ethoxide (compare Pechmann, Bauer, and Obermiller, Abstr., 1904, i, 592).

A comparison of the hydroxymethylene derivatives of the two acids shows a strong resemblance between them (compare Pechmann, Abstr., 1893, i, 401), but the condensation proceeds more easily with the benzene compound. *Ethyl hydroxymethylenehomophthalate*,

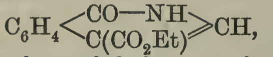
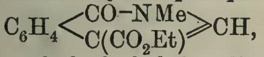
$$CO_2Et\cdot C_6H_4\cdot C(:CH\cdot OH)\cdot CO_2Et,$$

obtained in good yield from ethyl formate, ethyl homophthalate, and sodium as a colourless, viscid oil, is converted by heating at 100° in two hours into *ethyl* iso*coumarin-4-carboxylate*,



$$C_6H_4{<}\begin{matrix}CO\text{——}O\\C(CO_2Et)\end{matrix}{>}CH,$$

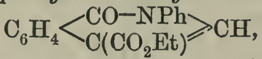
which crystallises in colourless needles from alcohol, m. p. 67—68°. Methyl-alcoholic potassium hydroxide hydrolyses it to formic and homophthalic acids. The corresponding *methyl* ester, $C_{11}H_8O_4$, forms colourless needles, m. p. 97°. iso*Coumarin-4-carboxylic acid*, $C_{10}H_6O_4$, obtained by warming the ester with concentrated hydrochloric acid, forms slender needles, m. p. 244°, and yields *iso*coumarin on heating with 50% sulphuric acid. This acid is similar to the corresponding 3-carboxylic acid (Bamberger and Frew, Abstr., 1894, i, 192), but its ready conversion into formic and homophthalic acids by alkali is in marked contrast with the isomeric acid.

Ethyl iso*carbostyril-4-carboxylate*,  $C_6H_4<\begin{matrix}CO—NH\\C(CO_2Et)\end{matrix}>CH$, prepared either from ethyl hydroxymethylenehomophthalate or from ethyl *iso*coumarincarboxylate by the action of ammonia, crystallises in colourless, slender needles, m. p. 227°. By shaking *iso*coumarin-4-carboxylic acid with ammonia and acidifying, iso*carbostyril-4-carboxylic acid*, $C_{10}H_7O_3N$, is obtained as needles from glacial acetic acid, m. p. 290° (decomp.). If, however, the ammonia is warmed, *iso*carbostyril is precipitated. *Ethyl 2-methyl*iso*carbostyril-4-carboxylate*,  $C_6H_4<\begin{matrix}CO-NMe\\C(CO_2Et)\end{matrix}>CH$, obtained from methylamine, crystallises from methyl alcohol in glistening needles, m. p. 98°. The corresponding *acid*, $C_{11}H_9O_3N$, forms small needles, m. p. 262°.

Aniline and ethyl hydroxymethylenehomophthalate form *ethyl anilinomethylenehomophthalate*,

$$CO_2Et\cdot C_6H_4\cdot C(:CH\cdot NHPh)\cdot CO_2Et,$$

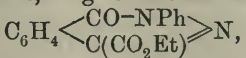
which crystallises in needles, m. p. 102·5°. By heating them together for a long time, *ethyl 2-phenyl*iso*carbostyril-4-carboxylate*,



$$C_6H_4<\begin{matrix}CO—NPh\\C(CO_2Et)\end{matrix}>CH,$$

is produced; it forms crystals, m. p. 118°. The parent *acid*, $C_{16}H_{11}O_3N$, forms microscopic needles, m. p. 267°.

Experiments were carried out in the hope that stereoisomerides of hydroxymethylenehomophthalic ester would exist, but only with partial success. By the action of *m*-nitrobenzoyl chloride on the sodium salt of methyl hydroxymethylenehomophthalate, two isomeric *m*-nitrobenzoates were obtained. The *a-compound*, $C_{19}H_{15}O_8N$, obtained when the dry sodium salt in ether is treated with *m*-nitrobenzoyl chloride, crystallises from methyl alcohol in prisms, m. p. 139°. The *β-compound*, formed when the aqueous solution is treated with the chloride, crystallises in slender needles, m. p. 98°, but experiments to transform the one isomeride into the other were without the desired result.

When ethyl hydroxymethylenehomophthalate is coupled with diazobenzene chloride, ring formation takes place, *ethyl 3-phenylphthalazone-1-carboxylate*,  $C_6H_4<\begin{matrix}CO—NPh\\C(CO_2Et)\end{matrix}>N$, being produced, which forms prisms, m. p. 115°.
W. R.

Methylenedioxyhydratropic Acid. Tiffeneau's Migration of the Phenyl Group. Paul Hoering (*Ber.*, 1908, 41, 3081—3084. Compare this vol., i, 497).—From the investigations of Tiffeneau, it was to be expected that derivatives of hydratropic acid could be prepared from α-ethoxy-α-phenylethylene, α-ethoxyanethole, and α-ethoxy*iso*safrole by acting on them with mercuric oxide and iodine in alcoholic solution and treating the ethoxyiodohydrins so formed with alcoholic potassium hydroxide. The experiments carried out with the first two substances were unsuccessful, but methylenedioxyhydratropic acid was prepared from *iso*safrole.

α-Methoxy*iso*safrole is converted by mercuric oxide and iodine in methyl alcohol into the *iodohydrin*, $CH_2{:}O_2{:}C_6H_3{\cdot}C(OMe)_2{\cdot}CHMeI$, which, however, could not be isolated, since it readily parts with iodine. The iodohydrin is converted by an alcoholic solution of potassium hydroxide into methylenedioxyhydratropic acid, $C_{10}H_{10}O_4$, m. p. 78·5—79°, identical with the acid obtained by Bougault from methylenedioxyhydratropaldehyde (Abstr., 1900, i, 495). α-Ethoxy*iso*safrole, when similarly treated, yields the same acid. W. H. G.

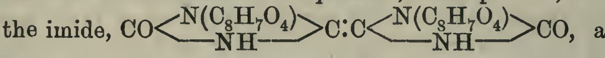
Nitration of Opianic Esters and Derivatives of Nitro-opianic Acid. Rudolf Wegscheider, Noel L. Müller, and Eduard Chiari (*Monatsh.*, 1908, **29**, 713—747).—Whilst ψ-methyl nitro-opianate, which is remarkable in having a m. p. (181·5—182·5°; Abstr., 1904, i, 59) higher than that of the corresponding acid, is readily prepared, the methyl ester is formed only with difficulty, and only one ethyl ester, of uncertain constitution, has as yet been obtained. It was therefore of interest to study the formation of nitro-opianates by the nitration of the esters of opianic acid by means of various nitrating agents. It is found that ψ-methyl nitro-opianate is obtained by nitration of either methyl opianate, the normal ester undergoing transformation during the reaction. Since the nitration of ψ-ethyl opianate leads similarly to the formation of the known ethyl nitro-opianate, this is probably the ψ-ester.

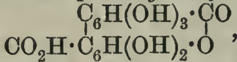
The action of acetyl nitrate on ψ-methyl opianate leads directly to the formation of ψ-methyl nitro-opianate, but on methyl opianate, to that of a *diacetate*, $NO_2{\cdot}C_6H(OMe)_2(CO_2Me){\cdot}CH(OAc)_2$, which separates from benzene in crystals, m. p. 159—160°, yields nitro-opianic acid on hydrolysis, is stable towards boiling methyl alcohol, and is hydrolysed only slowly by boiling water or hot $0{\cdot}1N$ potassium hydroxide; when heated with sodium methoxide or with hydrogen chloride in methyl-alcoholic solution, it is converted into ψ-methyl nitro-opianate, and, on treatment with concentrated aqueous ammonia, yields nitro-opianamide. These properties show that the diacetate cannot have the alternative constitution:

$$NO_2{\cdot}C_6H(OMe)_2[CH(OMe){\cdot}OAc]{\cdot}CO_2Ac.$$

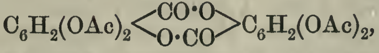
The *diacetate*, $C_{16}H_{19}O_{10}N$, formed by the action of acetyl nitrate, or of nitric acid and acetic anhydride in glacial acetic acid solution, on ethyl opianate, crystallises in colourless plates, m. p. 100—101°, and has properties resembling those of the preceding diacetate. When treated with methyl alcohol, the crude product from the action of acetyl nitrate on ethyl opianate is converted into ψ-methyl nitro-opianate.

Energetic nitration of the normal opianates by means of fuming nitric acid alone or in concentrated sulphuric acid solution leads to the formation of 4 : 5(or 5 : 6)-dinitro-2 : 3-dimethoxybenzoates (Wegscheider and Strauch, this vol., i, 794). *Ethyl dinitro-2 : 3-dimethoxybenzoate*, $C_{11}H_{12}O_8N_2$, crystallises from alcohol in white needles, m. p. 83·5—84·5°, and, on hydrolysis, yields an acid, m. p. 176—179°.

Nitro-opianic acid is now found to have the m. p. 169—170° (corr.). The *sodium* salt, $C_{10}H_8O_7NNa,4H_2O$, loses $4H_2O$ at 100°. The *anhydride*, $C_{20}H_{16}O_{13}N_2$, is formed together with the two methyl esters by the action of diazomethane on nitro-opianic acid; it separates from glacial acetic acid in crystals, m. p. 231—233°. The action of concentrated aqueous ammonia on nitro-opianic acid at the laboratory temperature leads to the formation of a *product*, decomp. 320°, which is probably the imide,  $CO<\begin{matrix}N(C_8H_7O_4)\\NH\end{matrix}>C{:}C<\begin{matrix}N(C_8H_7O_4)\\NH\end{matrix}>CO$, and may be identical with the substance described by Bistrzycki and Fink (Abstr., 1898, i, 427) as bisnitro-*m*-opindolone. G. Y.

Constitution of Tannin. N. Maximilian Nierenstein (*Ber.*, 1908, **41**, 3015—3019. Compare Abstr., 1905, 914; 1907, i, 331; this vol., i, 90).—When an aqueous solution of tannin is boiled with hydrogen peroxide, both ellagic acid and *pentahydroxydiphenylmethylolide-carboxylic acid* (*luteo-acid*),  $\begin{matrix}C_6H(OH)_3\cdot CO\\ | \qquad\quad |\\ CO_2H\cdot C_6H(OH)_2\cdot O\end{matrix}$, are formed. The latter is deposited, when the mother liquor from the ellagic acid is concentrated, as reddish-brown needles, which can be crystallised from pyridine and acetic acid. It turns brown at 305°, and decomposes at 338—342°. It dissolves in alkali hydroxide or hydrogen carbonate solutions, and also in concentrated sulphuric acid, and, when warmed with 10% sodium carbonate solution, yields its anhydride, ellagic acid.

The carboxyl group is eliminated when a pyridine solution of the luteo-acid is mixed with concentrated hydriodic acid and exposed to daylight for five days, pentahydroxydiphenylmethylolide being obtained.

Ellagic acid can be obtained by oxidising tetra-acetyldigallide with hydrogen peroxide, the reaction consisting in the elimination of two atoms of hydrogen and the union of the two benzene nuclei. *Tetra-acetyldigallide*,  $C_6H_2(OAc)_2<\begin{matrix}CO\cdot O\\O\cdot CO\end{matrix}>C_6H_2(OAc)_2$, crystallises from alcohol and acetic acid in needles, m. p. 130—132°.

J. J. S.

Halogen Amino-acids: 3 : 5-Dibromophenylalanine. Henry L. Wheeler and Samuel H. Clapp (*Amer. Chem. J.*, 1908, **40**, 337—348).—The authors propose to study the halogen derivatives of phenylalanine with the view of deciding the question of the position of halogens in proteins, and in the present paper the preparation of the 3 : 5-dibromo-derivatives is described.

3 : 5-*Dibromobenzyl bromide*, $C_6H_3Br_2\cdot CH_2Br$, prepared by adding bromine to 3 : 5-dibromotoluene at 170—180°, crystallises in prisms or long, felted needles, m. p. 95—96°, b. p. 173°/19 mm. and 169°/15 mm. It attacks the eyes violently. When heated with ethyl-sodio-

phthaliminomalonate (compare Sörensen, Abstr., 1903, i, 833), it yields *ethyl phthalimino-3 : 5-dibromobenzylmalonate*,

$$C_6H_4\colon(CO)_2\colon N\cdot C(CO_2Et)_2\cdot CH_2\cdot C_6H_3Br_2,$$

which forms aggregates of prisms and plates, m. p. 144—145°, and is hydrolysed by aqueous sodium hydroxide to *phthalamino-3 : 5-dibromobenzylmalonic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C(CO_2H)_2\cdot CH_2\cdot C_6H_3Br_2.$$

This forms snow-white, prismatic crystals, which lose carbon dioxide at 110°, or on boiling with water, with the production of *phthalamino-3 : 5-dibromobenzylacetic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_3Br_2,$$

crystallising in clusters of minute prisms, m. p. 174° (decomp.).

When boiled with 20% hydrochloric acid, this substance is resolved into phthalic acid and 92% of the theoretical quantity of *3 : 5-dibromophenylalanine*, $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot C_6H_3Br_2$; this dissolves in about 125 parts of water at 100°, and crystallises in long, hairy needles, m. p. 233—234° (decomp.). The aqueous solution tastes sweet and astringent. The substance is unchanged when heated with hydrochloric acid (D 1·19) in a sealed tube, but boiling aqueous barium hydroxide removes about 11% of the bromine. The *hydrochloride*, clusters of long prisms, changes on boiling with concentrated hydrochloric acid into stout prisms of a different habit, m. p. 254° (decomp.); the *barium* ($3H_2O$), *silver*, and *copper* ($1\frac{1}{2}H_2O$) salts are described; the *ethyl* ester is a viscid oil, b. p. 234—237°/24 mm., which forms a *picrate*, large, irregular prisms, m. p. 181—182°, and a *hydrochloride*, needle-like prisms, m. p. 186—187°.

The interaction of 3 : 5-dibromobenzyl bromide and ethyl sodiomalonate leads to the formation of *ethyl di-3 : 5-dibromobenzylmalonate*,

$$C(CH_2\cdot C_6H_3Br_2)_2(CO_2Et)_2,$$

crystallising in needle-like prisms, m. p. 99°.

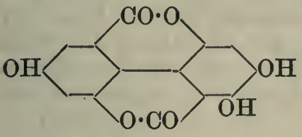
3 : 5-Dibromobenzylphthalimide, $C_6H_4\colon(CO)_2\colon N\cdot CH_2\cdot C_6H_3Br_2$, is formed by heating potassium phthalimide and 3 : 5-dibromobenzyl bromide to 140°. It crystallises in colourless prisms, m. p. 185°.

J. C. C.

Glycyrrhizic Acid. ALEXANDER TSCHIRCH and S. GAUCHMANN (*Arch. Pharm.*, 1908, **246**, 545—558).—The paper discusses (1) the distribution of glycyrrhizic acid in the vegetable kingdom; (2) the best methods of preparing the acid from Russian liquorice root or the "glycyrrhizinium ammoniacale" of commerce, and (3) the nature of the hydrolytic products of the acid. It was shown previously that on hydrolysis by boiling dilute sulphuric acid, glycyrrhizic acid yields glycyrrhetic and probably glycuronic acids (Tschirch and Cederberg, Abstr., 1907, i, 545). Larger quantities of the hydrolytic products have now been prepared, and exhaustive examination shows that the second product is undoubtedly glycuronic acid.

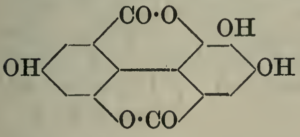
Glycyrrhetic acid, $C_{32}H_{48}O_7$, contains one ethylene linking, possesses neither methoxyl nor ethoxyl groups, furnishes a crystalline hydrocarbon (? naphthalene) on distillation with zinc dust, an aromatic oily product when distilled with soda-lime, and, on oxidation with permanganate, oxalic and picric acids. With nitric acid, no nitro-compound is formed, but only oxalic and picric acids. T. A. H.

Resoflavin. V. Lactone Dyes. JOSEF HERZIG and S. EPSTEIN (*Monatsh.*, 1908, 29, 661—675).—In the constitution ascribed to resoflavin by Herzig and Tscherne (this vol., i, 547) there remains doubtful whether one of the hydroxyls occupies the position 2 or 4. The analogy of the formation of resoflavin from 3:5-dihydroxybenzoic acid with that of flavellagic acid from gallic acid makes it probable that the hydroxyl in question occupies position 4, resoflavin having therefore the annexed constitution.



The behaviour of resoflavin when fused with potassium hydroxide is now found to be in agreement with this view of its constitution. Barth and Goldschmiedt (Abstr., 1879, 930) showed that ellagic acid, on fusion with potassium hydroxide, yields hexahydroxydiphenyl, pentahydroxydiphenylmethylolide (Graebe, Abstr., 1903, i, 262; Perkin and Nierenstein, Trans., 1905, 87, 1412) being formed intermediately. Resoflavin, on the other hand, when treated in the same manner, yields 3:5-dihydroxybenzoic acid, m. p. 237—240° (232—233°: Böttinger, this Journ., 1875, 567); the methyl ester, m. p. 163—165° (60°: Meyer, Abstr., 1901, i, 628). 3:5-Dimethoxybenzoic acid, m. p. 185—186° (175—176°: Tiemann and Streng, Abstr., 1882, 51); the methyl ester, m. p. 42—44° (81°: Meyer, Abstr., 1888, 148).

As ellagic acid, which contains two pyrogallol groups, yields hexahydroxydiphenyl, and, as the resorcinol nucleus is more stable than the pyrogallol nucleus towards fused alkalis, a substance having the annexed constitution must under the same conditions yield pentahydroxydiphenyl. The degradation of resoflavin to 3:5-dihydroxybenzoic acid must be explained, therefore, by the presence of a resorcinol and a hydroxyquinol grouping, the latter being more unstable towards the fused alkali than the carboxyl attached to the resorcinol portion of the complex.



When heated on the water-bath with alcoholic sulphuric acid, the ether ester of resoflavin yields a white *substance*, which, on treatment with diazomethane, forms trimethylresoflavin, and hence is the hydrolysis product of this ether. The ether acid,

$$C_{12}H_3(OMe)_5(CO_2H)_2,$$

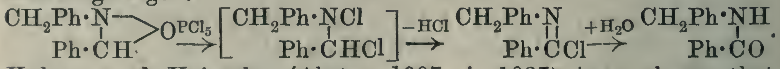
and trimethylresoflavin must be formed intermediately. In agreement with this, methyl 2:3:4:4′:5′:6′-hexamethoxydiphenyl-6:2′-carboxylate (Herzig and Pollak, this vol., i, 546), when treated with alcoholic sulphuric acid in the same manner, yields a yellow, crystalline *substance*, m. p. above 300°, which contains a slightly smaller percentage of methoxyl than tetramethylellagic acid, into which it is converted by the action of diazomethane.

G. Y.

Nature and Constitution of Rhizocholic Acid. Hugo Schrötter and Richard Weitzenböck (*Monatsh.*, 1908, **29**, 749—751).—It is now found that the acid obtained by the successive action of sulphuric and nitric acids on cholesterol, cholic acid, camphor, or turpentine oil, and previously termed rhizocholic acid (this vol., i, 532, 636), is benzenepentacarboxylic acid. When heated it sublimes, losing carbon dioxide and forming pyromellitic anhydride. It is considered that the pentacarboxylic acid is a secondary product, formed by oxidation of primarily liberated carbon. Its formation, therefore, cannot be looked upon as evidence of any relationship between cholesterol and cholic acid, on the one hand, and the terpenes, on the other. G. Y.

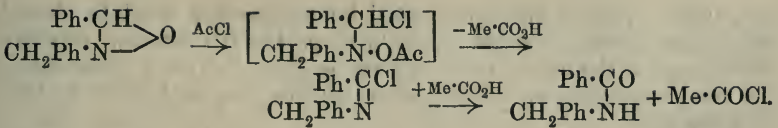
Action of Hydrogen Persulphide on Organic Compounds. Heinrich Brunner and V. Vuilleumier (*Chem. Zentr.*, 1908, ii, 588; from *Schweiz. Woch. Chem. Pharm.*, 1908, **46**, 436—438).—The authors have obtained the following substances by adding hydrogen persulphide to a solution of the organic compound in carbon disulphide, chloroform, or benzene. From *benzaldehyde*, long, colourless, prismatic crystals of the composition $(Ph\cdot COH)_2,H_2S_3$, which decompose at 28° into sulphur, hydrogen sulphide, and benzaldehyde. *Anisaldehyde*, similar crystals of the composition $(OMe\cdot C_6H_4\cdot COH)_2,H_2S_3$, decomposing at 18°. *Cinnamaldehyde* gives a solid, non-crystallisable product, C_9H_8O,H_2S_4. *Benzoquinone*, a violet powder of the composition $(C_6H_4O_2)_4,H_2S_5$, which is possibly a mixture of $(C_6H_4O_2)_2,H_2S_2$ and $(C_6H_4O_2)_2,H_2S_3$. Piperidine in chloroform gives a red solution with sulphur, which, on addition of carbon disulphide, yields $C_5H_{11}N\cdot CS\cdot S\cdot NHC_5H_{11}$. Many aldehydes and ketones simply cause the precipitation of white, prismatic sulphur. The compounds obtained with strychnine and brucine were found to be identical with those described by Hoffmann and Schmidt (Abstr., 1877, ii, 789, 905). J. V. E.

Molecular Rearrangement of *N*-Benzylaldoxime. Mitsuru Kuhara (*J. Coll. Sci. Tōkyō*, 1908, **25**, xviii, 1—4).—The author has succeeded in isolating benzoylbenzylamine iminochloride (compare Pechmann and Heinze, Abstr., 1897, i, 515) as an intermediate product of the rearrangement of *N*-benzylbenzaldoxime by the action of phosphorus pentachloride, and in converting the iminochloride into benzylbenzamide by the action of water. The transformation of *N*-benzylbenzaldoxime into benzylbenzamide under the influence of phosphorus pentachloride, therefore, probably takes place through the following stages:



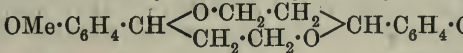
$$\left.\begin{matrix}\mathrm{CH_2Ph\cdot N}\\ |\\ \mathrm{Ph\cdot CH}\end{matrix}\right>\mathrm{O}\xrightarrow{\mathrm{PCl_5}}\left[\begin{matrix}\mathrm{CH_2Ph\cdot NCl}\\ |\\ \mathrm{Ph\cdot CHCl}\end{matrix}\right]\xrightarrow{-\mathrm{HCl}}\begin{matrix}\mathrm{CH_2Ph\cdot N}\\ \|\\ \mathrm{Ph\cdot CCl}\end{matrix}\xrightarrow{+\mathrm{H_2O}}\begin{matrix}\mathrm{CH_2Ph\cdot NH}\\ |\\ \mathrm{Ph\cdot CO}\end{matrix}.$$

Kuhara and Kainosho (Abstr., 1907, i, 1027) have shown that phenylbenzamide is formed by the action of acetic acid on chlorobenzylideneaniline. It is therefore probable that the rearrangement of *N*-benzylbenzaldoxime by the action of acetyl chloride takes place thus:



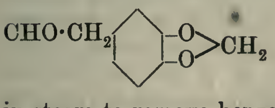
$$\begin{matrix}\text{Ph}\cdot\text{CH}\\ | \\ \text{CH}_2\text{Ph}\cdot\text{N}\end{matrix}\!>\!\text{O} \xrightarrow{\text{AcCl}} \left[\begin{matrix}\text{Ph}\cdot\text{CHCl}\\ | \\ \text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{OAc}\end{matrix}\right] \xrightarrow{-\text{Me}\cdot\text{CO}_2\text{H}} \begin{matrix}\text{Ph}\cdot\text{CCl}\\ \| \\ \text{CH}_2\text{Ph}\cdot\text{N}\end{matrix} \xrightarrow{+\text{Me}\cdot\text{CO}_2\text{H}} \begin{matrix}\text{Ph}\cdot\text{CO}\\ | \\ \text{CH}_2\text{Ph}\cdot\text{NH}\end{matrix} + \text{Me}\cdot\text{COCl}.$$

W. H. G.

β-*p*-Methoxyphenylpropaldehyde obtained from the Isomeric α-*p*-Methoxyphenylpropylene-αβ-glycols [α-*p*-Methoxyphenylpropane-αβ-diols]. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 259—269).—According to Tiffeneau and Daufresne (Abstr., 1907, i, 701), the β-modification of α-*p*-methoxyphenylpropylene-αβ-glycol (compare Balbiano, Abstr., 1907, i, 522) yields *p*-methoxyphenylacetone when dehydrated by means of 20% sulphuric acid. The author shows, however, that the compound is not a ketone, but β-*p*-methoxyphenylpropaldehyde, which is also obtained by dehydrating the isomeric α- and β-glycols by means of zinc chloride (compare Balbiano and Paolini, Abstr., 1906, i, 186). When either method of dehydrating the glycol is used, this aldehyde is accompanied by a small quantity of a *dimeric* form,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\!<\!\begin{matrix}\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\\ \text{CH}_2\cdot\text{CH}_2\cdot\text{O}\end{matrix}\!>\!\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ (?), which crystallises from alcohol in microscopic prisms, m. p. 181—182°, has the normal molecular weight in freezing benzene, and exhibits no aldehydic properties. When treated with benzenesulphonylhydroxamic acid, the α- or β-form of β-*p*-methoxyphenylpropaldehyde yields a small amount of the corresponding hydroxamic acid, which was separated as *copper* salt, $C_{10}H_{11}O_3NCu$; when dissolved in dilute hydrochloric acid, this salt gives an intense violet coloration with ferric chloride, whilst, on hydrolysis, it yields anisic acid and a small quantity of a *substance*, $C_6H_7O_4N$, crystallising in shining laminæ, m. p. about 150°. T. H. P.

Constituents of Ethereal Oils. Homopiperonal and its Derivatives. FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1908, **41**, 2751—2753).—To distinguish between the aromatic constituents of ethereal oils containing an allyl or a propenyl group in the side-chain, the authors oxidise the substance with ozone, whereby rupture at the double linking occurs, with the formation of an aldehyde if a propenyl group is present, whilst the corresponding homo-derivative is obtained if an allyl group is present:

$$\text{R}\cdot\text{CH:CHMe} \longrightarrow \text{R}\cdot\text{CHO};\ \text{R}\cdot\text{CH}_2\cdot\text{CH:CH}_2 \longrightarrow \text{R}\cdot\text{CH}_2\cdot\text{CHO}.$$



Homopiperonal (annexed constitution), m. p. 69°, b. p. 143—144°/10 mm., D_{20} 1·295, n_D 1·57117, is obtained by passing ozone through a solution of safrole in benzene mixed with a small quantity of water, distilling the product in steam to remove benzene and unchanged safrole, and extracting the non-volatile aldehyde with ether. The *semicarbazone*, m. p. 189°, *oxime*, m. p. 124—125°, b. p. 180—181°/10 mm., and *nitrile*, b. p. 153—156°/10 mm., D_{20} 1·231, n_D 1·53698, are described. Hydrolysis of the last by 10% alcoholic potassium hydroxide yields *homopiperonylic acid*, $C_9H_8O_4$, m. p. 127°, the *methyl* ester of which has b. p. 153—155°/10 mm.,

D_{20} 1·246, n_D 1·534, and is converted by sodium and absolute alcohol into *homopiperonyl alcohol*, $C_9H_{10}O_3$, b. p. 156°/10 mm., n_D 1·54780. By reduction, the nitrile yields the *amine*, $C_9H_{11}O_2N$, b. p. 146—148°/10 mm., D_{20} 1·225, n_D 1·5620, of which the *picrate* has m. p. 160° (decomp.). C. S.

Quinone Formation. RAYMOND VIDAL (*Chem. Zentr.*, 1908, ii, 240; from *Mon. Sci.*, 1908, [iv], 22, i, 368—372).—Quinone formation is considered as supporting the views expressed (Abstr., 1907, i, 1020) on the nature of the benzene ring. J. V. E.

Action of Piperidine on *l*-Pinene Chloroxime. P. G. GOLUBEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1015—1018).—The action of piperidine on the chloroxime of *l*-pinene isolated from the ethereal oil of the Siberian fir proceeds in two directions: (1) $C_{10}H_{16}\cdot NOCl + C_5H_{11}N = HCl + C_{10}H_{16}NO\cdot C_5H_{10}N$, yielding a compound identical with that given by *d*-pinene from American turpentine;

(2) $C_{10}H_{16}\cdot NOCl + C_5H_{11}N = HCl + C_5H_{11}N + C_{10}H_{15}ON$,

yielding the nitrosopinene obtained by the action of diethylamine on *d*-pinene chloroxime. T. H. P.

Essential Oil of French Parsley and the Contained Ether, 2:3:4:5-Tetramethoxy-1-allylbenzene. HERMANN THOMS (*Ber.*, 1908, 41, 2753—2761. Compare Abstr., 1904, i, 47).—Experiments are in progress to ascertain whether the climate, the conditions of cultivation, or the degree of ripeness of the seeds, accounts for the fact that the essential oil of French parsley contains a large quantity of myristicin and a small amount of apiole, whilst the oil from German parsley is rich in the latter.

A large quantity of the oil of French parsley has been freed from phenols and acids, and the resulting liquid separated into two fractions, b. p. 160—165°/15 mm. and 165—170°/15 mm. The presence of myristicin in both is proved by the formation of dibromomyristicin dibromide (Abstr., 1904, i, 47), but a Zeisel estimation indicates the presence of a substance richer in methoxyl groups. This substance, ultimately isolated by the aid of solid carbon dioxide, has been proved to be 2:3:4:5-*tetramethoxy*-1-*allylbenzene*, m. p. 25°, D^{25} 1·087, n^{25}_D 1·51462. The presence of the allyl group is indicated by the dispersion and the molecular refraction, and by the formation of a red coloration with phloroglucinol and hydrochloric acid (compare Kobert, *Zeitsch. anal. Chem.*, 1908, 47, 711). The positions of the methoxyl groups are determined by oxidation with potassium permanganate, whereby 2:3:4:5-*tetramethoxybenzoic acid*, m. p. 87°, is obtained, and also by successive treatment with alcoholic potassium hydroxide (which changes the allyl to a propenyl group), reduction with sodium and alcohol, and nitration of the product, resulting in the formation of 4-nitro-2:3:5-trimethoxy-1-propylbenzene (Abstr., 1903, i, 558). By nitration, the methoxyl group in position 4 has been replaced by a nitro-group (compare Thoms and Herzog, Abstr., 1903, i, 415).

The same operations on the above-mentioned fractions yield the same compounds, as also does the oil from French parsley seeds grown in Dahlem. C. S.

Ethereal Oil from Salvia sclarea. ROURE-BERTRAND FILS (*Chem. Zentr.*, 1908, ii, 323; from *Wiss. ind. Ber. Roure-Bertrand Fils*, 1908, [ii], 7, 10—11).—The oil distilled in 1904 (*Chem. Zentr.*, 1906, ii, 535) has been saponified, and *l*-linalool is found to be the chief constituent, together with some resinous substances which render it insoluble in 96% alcohol, acetone, methyl alcohol, &c. J. V. E.

Resin of Antiaris toxicaria. ADOLPH WINDAUS and A. WELSCH (*Arch. Pharm.*, 1908, **246**, 504—508. Compare de Vrij and Ludwig, *Sitz. Wien. Akad.*, 1868, **57**, 56, and Kiliani, Abstr., 1897, i, 91).—The portion of the latex of *Antiaris toxicaria* soluble in light petroleum is composed principally of the *cinnamic* ester of *α-amyrin*, $C_{39}H_{56}O_2$, m. p. 176°, $[\alpha]_D^{25}$ +78°45′ (in chloroform), which crystallises from methyl alcohol in long, thick, colourless needles. From the products of hydrolysis of the amorphous portion of the resin, α-amyrin, cinnamic acid, and some stearic acid were obtained. No β-amyrin seems to be present in the resin. T. A. H.

Decomposition of Amygdalin by Emulsin. KARL FEIST (*Arch. Pharm.*, 1908, **246**, 509—510. Compare this vol., i, 437, and Rosenthaler, *ibid.*, i, 817).—Rosenthaler's observation, that emulsin is capable of forming *d*-benzaldehydecyanohydrin from benzaldehyde and hydrocyanic acid, is, contrary to that author's opinion, in reality a confirmation of Feist's statement that *d*-benzaldehydecyanohydrin is the first product of the action of emulsin on amygdalin, since the action probably reaches equilibrium in the two directions: *d*-benzaldehydecyanohydrin + emulsin $\rightleftharpoons$ benzaldehyde + hydrocyanic acid + emulsin. T. A. H.

New Glucoside (Erytaurin) obtained from the Common Century. HENRI HÉRISSEY and L. BOURDIER (*J. Pharm. Chim.*, 1908, [vi], **27**, 252—255).—The glucoside, obtained from the plant by a lengthy extraction process, crystallises in small, colourless prisms on addition of ether to its solution in a mixture of chloroform and alcohol. It is bitter to the taste, has $[\alpha]_D - 131\cdot6°$ to $-134\cdot4°$, does not reduce Fehling's solution, but gives a blue coloration with a mixture of ferric chloride and potassium ferricyanide. Erytaurin is slowly hydrolysed by emulsin, yielding dextrose and a pale yellow precipitate. T. A. H.

Glucosides of Linaria. TIMOTHÉE KLOBB (*Bull. Soc. chim.*, 1908, [iv], **3**, 858—872. Compare Abstr., 1907, i, 864; ii, 123).—The yield of linarin from the dried flowers of *Linaria vulgaris* amounts to 1·5—2·8%; it may be recrystallised from 50% acetic acid. Saturated solutions in boiling alcohol contain 0·30% of linarin; in cold alcohol, 0·24%; in boiling 50% acetic acid, 0·57%, and in the cold acid, 0·36%. The glucoside apparently forms an additive compound with phenol, and is readily absorbed from solution by animal charcoal. β-Linarin has m. p. 257—260°, and is more soluble than linarin in 50% acetic acid.

α-Pectolinarin is straw-yellow and amorphous, but sometimes forms hard, almost white, semi-crystalline aggregates. Saturated solutions in alcohol at 80° contain 0·582% of pectolinarin; in cold alcohol, 0·097%; in water at 100°, 0·24%. Pectolinarin is rapidly hydrolysed by dilute acids at 85°, giving a mixture of the two phenols. Both linarin and pectolinarin, when hydrolysed by concentrated hydrochloric acid, give linaric phenol only.

Linaric phenol crystallises from glacial acetic acid in needles or orange-red prisms, the latter containing both water and acetic acid of crystallisation, which are lost at 120—130°. Its m. p. is 277—279°, not 245° as stated previously; it gives a greenish-black coloration with alcoholic ferric chloride, and a greenish-grey precipitate with chloroform and potassium hydroxide, becoming reddish-brown on exposure to the air. It forms an *acetate*, $C_{19}H_{11}O_7Ac_3$, m. p. 248—250°.

Anhydrolinaric phenol is quite stable towards alkali hydroxides (difference from linaric phenol), gives a violet-brown coloration with alcoholic ferric chloride, a bright red coloration with chloroform and potassium hydroxide, and a brown coloration in Liebermann's reaction. The *acetate* forms colourless needles, m. p. 198—200°, and the *benzoate*, $C_{19}H_{10}O_6(COPh)_2$, short, white needles, m. p. 199—201°. E. H.

Oleoeuropein; a New Glucoside obtained from the Olive, Olea Europa. ÉMILE BOURQUELOT and J. VINTILESCO (*Compt. rend.*, 1908, **147**, 533—535; *J. Pharm. Chim.*, 1908, [vi], **28**, 303—314). [Compare Power and Tutin, Trans., 1908, **93**, 891, 904.] —Bourquelot's biological test (Abstr., 1902, ii, 55) for the detection of glucosides shows the presence of a glucoside, *oleoeuropein*, hydrolysable by emulsin in the fruits, leaves, and bark of the olive. This substance, which was only obtained as a slightly yellow powder, possesses a bitter taste, is readily soluble in cold water or warm alcohol, insoluble in ether, and has $[\alpha]_D - 5·166°$. It reduces Fehling's solution on boiling, and its solution in water is coloured yellow by alkalis, red by sulphuric acid, and green by ferric chloride. The glucoside is hydrolysed by emulsin or by boiling with acids, yielding dextrose. Emulsin also occurs in the leaves and fruit of the olive. T. A. H.

***l*-Arabinose and Dextrose as Inversion Products of Saponin from the Leaves of Polyscias nodosa, Forst.** A. W. VAN DER HAAR (*Pharm. Weekblad*, 1908, **45**, 1184—1191).—Anhydrous saponin from the leaves of *Polyscias nodosa* has the empirical constitution $C_{25}H_{42}O_{10}$, and contains an arabinose complex. On inversion, it takes up water, yielding *l*-arabinose, dextrose, and sapogenin. A. J. W.

The Hydrocarbon Nucleus of Frangula emodin, Aloe-emodin, and Rhein. OTTO A. OESTERLE and ED. TISZA (*Arch. Pharm.*, 1908, **246**, 432—436).—A continuation of work on the constitution of the emodins obtained from the bark of *Rhamnus frangula* and from aloes respectively, showing that the former is a β-methylanthracene derivative as already formulated (this vol., i, 350), and the latter probably derived from α-methylanthracene.

Frangula emodin, on distillation with zinc dust, yields β-methylanthracene (compare Liebermann, this Journ., 1876, i, 251; Perkin and Hummel, Trans., 1894, **65**, 924).

The hydrocarbon obtained when aloe-emodin is distilled with zinc dust forms greenish-yellow leaflets, has m. p. 208—209°, fluoresces green in acetic acid, gives a blood-red *picric acid* compound, m. p. 145°, and is polymerised in benzene solution on exposure to sunlight, yielding a *hydrocarbon*, m. p. 256°, crystallising in colourless needles. Since these characteristics are different from those of β-methylanthracene, the authors suggest that the hydrocarbon thus obtained from aloe-emodin is probably α-methylanthracene.

Rhein on distillation with zinc dust yields anthracene (compare Hesse, Abstr., 1900, i, 41; Tschirch and Heuberger, Abstr., 1903, i, 107; Oesterle, Abstr., 1904, i, 80). T. A. H.

Pimpinellin. JOHANNES HERZOG and V. HÂNCU (*Arch. Pharm.*, 1908, **246**, 402—414. Compare Heut, Abstr., 1898, i, 598).—The preparation of pimpinellin from the root of *Pimpinella saxifraga* has been simplified, the characters of the substance definitely determined, and its oxidation by hydrogen peroxide studied. The results of this work indicate that pimpinellin is a naphthalene derivative.

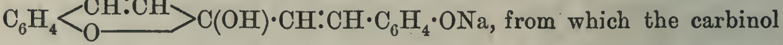
Pimpinellin, $C_{13}H_{10}O_5$, m. p. 119°, obtained to the extent of 0·5% by extracting the ground root with benzene and treating the concentrated extract with light petroleum, crystallises in glancing, white needles, sublimes with slight decomposition, and becomes yellow on long exposure to light. It is probably a lactone, contains two methoxyl groups, and, on oxidation with hydrogen peroxide, furnishes a *tribasic acid*, $C_9H_6O_8$, m. p. 220° (decomp.). This crystallises in short, thick needles from acetic acid, is readily soluble in alcohol, less so in water, and can be sublimed, forming, then, long needles recalling those of phthalic anhydride, which it resembles in giving a fluorescein reaction. The acid contains no methoxyl groups; it yields a well-crystallised *pyridine* salt, m. p. 179° (decomp.), and this reacts with diphenylcarbamyl chloride (compare this vol., i, 268) to form the *diphenylated acid amide*, $C_6H_3O_2(CO\cdot NPh_2)_3$, m. p. 224·5—225·5°, which separates from boiling alcohol or toluene in splendid pale yellow crystals.

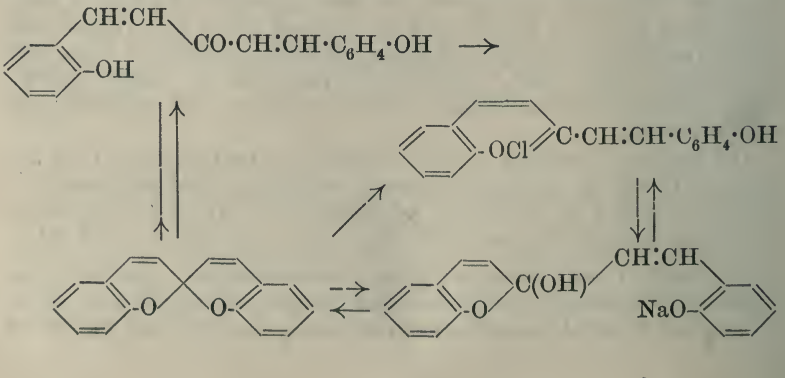
The second crystalline product isolated by Heut (*loc. cit.*) from the roots could not be obtained, although evidence of the existence of a minute quantity of a second substance, possibly a decomposition product of pimpinellin, was observed. T. A. H.

Formation and Chemistry of Anthocyanins. LEOPOLD VON PORTHEIM and EMIL SCHOLL (*Ber. deut. bot. Ges.*, 1908, **26a**, 480—483).—Pure solutions of unstable, plant-colouring matters, such as that of beetroot, can be prepared by dialysing the expressed juice or an aqueous extract of the plant (compare Weigert, Abstr., 1896, i, 387).

The colouring matter of the testa of the seed of *Phaseolus multiflorus* is insoluble in water. An alcoholic extract of the testæ deposits on slight concentration a small quantity of a yellow *substance*, crystallising in microscopic bundles of needles. The mother liquor from this deposits no more crystalline matter on further concentration, but, when boiled with a few drops of hydrochloric acid, yields a reddish-violet liquid, which, after some days, deposits ruby-red, microscopic crystals of a *substance*, readily soluble in alcohol, and turning blue on addition of ammonia.

The mother liquor referred to above may also be separated into three fractions by treatment with ether. Of these, (*A*) is a viscid, brown mass, which yields the crystalline, red colouring matter on hydrolysis by acids; (*B*) a reddish-violet, amorphous product, and (*C*) a brownish-yellow residue, insoluble in water. T. A. H.

Cyclic Oxonium Salts from Disalicylideneacetone, and *spiro*Pyran Derivatives. Herman Decker and Heinrich Felser (*Ber.*, 1908, **41**, 2997—3007).—Tiemann and Kees' disalicylideneacetone (dicoumaro-ketone) (Abstr., 1885, 1073) is very easily obtained, in the form of the alkali salt, by adding alcoholic potassium hydroxide (3—4 mols.) to an alcoholic solution of salicylaldehyde (2 mols.) and acetone (rather less than 1 mol.). By treating an alcoholic solution of the ketone with hydrogen chloride or 50% sulphuric acid, a red solution of the 2-*o*-hydroxystyrylbenzopyrylium salt is obtained, from which ferric chloride precipitates the dark red *ferrichloride*, $C_{17}H_{13}O_2Cl_4Fe$, m. p. 180°. The very intense colour of these oxonium salts is due, in part, to the presence of the *o*-hydroxystyryl group. The red oxonium chloride gives with 10% sodium hydroxide a yellow solution of the *sodium* salt of 2-*o*-hydroxystyrylbenzopyranol-2,  $C_6H_4{<}\begin{matrix}CH{:}CH\\ O\end{matrix}{>}C(OH)\cdot CH{:}CH\cdot C_6H_4\cdot ONa$, from which the carbinol itself cannot be isolated, since the carbinol and the phenolic hydroxyl groups eliminate water, and the stable, colourless, crystalline *dibenzo*spiro*pyran*, m. p. 102°, is formed, just as the carbinols of other cyclic oxonium salts react with alcohols to give ethers (Decker and



von Fellenberg, Abstr., 1907, i, 950). By treatment with concentrated acids, one pyran ring of the *spiro*pyran derivative is readily ruptured, yielding the coloured 2-*o*-hydroxystyrylbenzopyrylium salt, whilst warm alcoholic sodium hydroxide opens both rings, with the regeneration of disalicylidineacetone.

The constitutions and the transformations of the preceding compounds are indicated in the preceding scheme.

These changes are not readily explicable by Bülow's benzopyranol-(4) formula (Abstr., 1901, i, 400, 559; 1902, i, 113).

Perkin, Robinson, and Turner (Trans., 1908, **93**, 1088), criticising Decker's formula of the benzopyrylium salts, contend that with this formula these should not be so highly coloured as they actually are, since the linkings in the skeleton formula are in a similar position to those in quinoline; they suggest an alternative *o*-quinonoid formula. The authors argue that this formula does not explain the formation of benzopyrylium salts from coumarin, the ready hydrolysis of the carbinol, the colour of the salts, and the absence of colour in the carbinol. It is known that in acridinium and xanthylium salts the replacement of the NMe group by O in the ring intensifies the colour. Just the same difference occurs with benzopyrylium and quinolinium salts, and the deeper colour of the former is regarded as a proof that they are oxonium salts isologous with quinolinium salts.

2-*o*-Hydroxystyrylbenzopyrylium chloride, $C_{17}H_{13}O_2Cl,H_2O$, forms red needles with a bronze-green reflex, and, from its moderately-concentrated solution, other crystalline salts and double salts can be obtained. Dibenzo*spiro*pyran is formed when disalicylideneacetone is kept above its m. p., 168°, for ten minutes. C. S.

Brazanquinones. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1908, **41**, 2800—2802).—As catechone trimethyl ether yields a well-crystallised nitro-derivative, the authors have investigated the action of nitric acid on the closely-allied 2 : 7 : 8-trimethoxybrazanquinone (this vol., i, 672), and find that it gives a trinitro-derivative; similarly, 2-methoxybrazanquinone yields a dinitro-derivative.

Trinitro-2 : 7 : 8-*trimethoxybrazanquinone*, $C_{19}H_{11}O_{12}N_3$, prepared by adding the quinone to nitric acid (D 1·5), crystallises in orange-yellow needles, m. p. 275° (decomp.). 1 : 3(?)-*Dinitro*-2-*methoxybrazanquinone* forms small, stout crystals, m. p. 253—254° (decomp.). In order further to characterise 2-methoxybrazanquinone, the authors have converted it by reduction and simultaneous acetylation into 5 : 10-*diacetoxy*-2-*methoxybrazan*, which crystallises in white, prismatic needles, m. p. 195—196°. Its solution in concentrated sulphuric acid is green, and shows an intense dark green fluorescence.

5 : 10-Diacetoxy-2 : 7 : 8-trimethoxybrazan (Kostanecki and Lloyd, Abstr., 1903, i, 646) gives the same colour reaction. When boiled with alcoholic potash and the product treated with dimethyl sulphate, 5 : 10-diacetoxy-2-methoxybrazan yields 2 : 5 : 10-*trimethoxybrazan*, crystallising in white leaflets, m. p. 165°. This shows the same colour reaction with sulphuric acid as the compound just described, and its alcoholic solution exhibits a weak blue fluorescence. J. C. C.

Morphine. XIX. Relationship between ψ-*apo*Codeine and *apo*Morphine. LUDWIG KNORR and FELIX RAABE (*Ber.*, 1908, **41**, 3050—3054).—ψ-*apo*Codeine (Abstr., 1907, i, 790) stands in the same relationship to *apo*morphine as codeine to morphine; it is thus the 3-methyl ether of *apo*morphine, and is identical with Pschorr, Jäckel, and Fecht's methyl ether (Abstr., 1903, i, 193). The crystals obtained from alcoholic solutions contain 1EtOH, and melt and decompose at 105°, after sintering at 100°. In alcoholic solution it has $[\alpha]_D^{15}$ $-90°$ ($c = 0{\cdot}84$), and in chloroform solution, $-103°$ ($c = 2{\cdot}6$). The dimethyl ether of *apo*morphine has not been obtained crystalline, even after distillation under reduced pressure. It has b. p. 195—205° in the cathode ray vacuum, and $[\alpha]_D^{15}$ $-148°$ ($c = 1{\cdot}6395$) in alcoholic solution. The *hydriodide*, $C_{19}H_{22}O_2NI$, forms pale yellow prisms, m. p. about 220°.

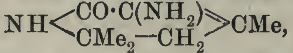
The rotatory power of methyl-*apo*morphine methiodide is $[\alpha]_D^{15}$ $-20°$ ($c = 1{\cdot}2573$) in methyl-alcoholic solution. Diacetylmethyl*apo*morphine has m. p. 130°. J. J. S.

Protopine of Japanese Corydalis Roots (Corydalis Vernyi). K. MAKOSHI (*Arch. Pharm.*, 1908, **246**, 401—402).—The root of this plant contains two alkaloids, the one, identical with protopine, occurring to the extent of 0·13%, and the other, obtained in the form of a yellow, crystalline mass and closely resembling dehydrocorydaline in appearance and properties, is present to the extent of 0·013%.

T. A. H.

Certain *o*-Amino- and *o*-Hydroxy-ketohydropyridines. I. GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1908, **43**, 890—912).—The author describes various amino- and the corresponding hydroxytetrahydropyridine derivatives in which the amino- (or hydroxy-) group is in the 3 position, whilst the 2-position is occupied by what is most probably a carbonyl group.

3-*Amino*-4 : 6 : 6-*trimethyl*-Δ^3-*tetrahydro-2-pyridone*,



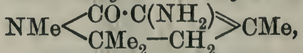
$$\mathrm{NH}\left<\begin{array}{l}\mathrm{CO{\cdot}C(NH_2)}\\ \mathrm{CMe_2{-}CH_2}\end{array}\right>\mathrm{CMe},$$

prepared by converting 4 : 6 : 6-trimethyl-Δ^3-tetrahydro-2-pyridone-3-carboxylamide (compare this vol., i, 679) into the corresponding bromoamide by means of potassium hypobromite and then boiling with water, separates from benzene in friable, prismatic crystals, m. p. 130—131°, exhibiting a slight blue fluorescence, and yields an alkaline aqueous solution, which with ferric chloride gives an orange-red and, later, a blood-red coloration. Its *platinichloride*,

$$(C_8H_{14}ON_2)_2,H_2PtCl_6,$$

m. p. 235°, is decomposed when boiled with water, giving the corresponding hydroxy-compound (*vide infra*), $(C_8H_{14}ON_2)_2,H_2PtCl_6 + 2H_2O = 2C_8H_{13}O_2N + (NH_4)_2PtCl_6$. The hydroxy-compound is also formed by the action of nitrous acid on the amino-derivative.

3-*Amino*-1 : 4 : 6 : 6-*tetramethyl*-Δ^3-*tetrahydro-2-pyridone*,



$$\mathrm{NMe}\left<\begin{array}{l}\mathrm{CO{\cdot}C(NH_2)}\\ \mathrm{CMe_2{-}CH_2}\end{array}\right>\mathrm{CMe},$$

prepared from 1 : 4 : 6 : 6-tetramethyl-Δ^3-tetrahydro-2-pyridone-3-

carboxylamide (*loc. cit.*), crystallises from ether in colourless or faintly yellow prisms, m. p. 60—61°, has an alkaline reaction, shows normal cryoscopic behaviour in benzene, and reacts with water or nitrous acid like the preceding compound. The *platinichloride*,

$$(C_9H_{16}ON_2)_2,H_2PtCl_6,H_2O,$$

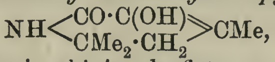
has m. p. 196—197° (decomp.).

Both these amino-compounds are mono-acid bases rather weaker than ammonia; they do not absorb carbon dioxide from the air, but precipitate aluminium hydroxide from solutions of aluminium salts. The most striking properties of the bases are the ease with which they react with nitrous acid and the mobility of the amino-group towards hydrolysts, these being due to the presence of the group

$$\cdot CR{:}C(NH_2)\cdot CO\cdot$$

in a hydrogenated nucleus. They both readily reduce Fehling's solution, ammoniacal silver nitrate solution, &c.

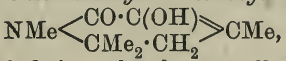
3-*Hydroxy*-4 : 6 : 6-*trimethyl*-Δ^3-*tetrahydro*-2-*pyridone*,



$$NH{<}\begin{array}{l}CO\cdot C(OH)\\CMe_2\cdot CH_2\end{array}{>}CMe,$$

crystallises from water in shining leaflets, m. p. 143°, has a neutral reaction, gives a blue coloration with ferric chloride, and readily reduces Fehling's solution, ammoniacal silver nitrate solution, &c.

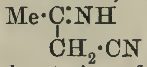
3-*Hydroxy*-1 : 4 : 6 : 6-*tetramethyl*-Δ^3-*tetrahydro*-2-*pyridone*,



$$NMe{<}\begin{array}{l}CO\cdot C(OH)\\CMe_2\cdot CH_2\end{array}{>}CMe,$$

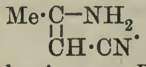
crystallises from alcohol in colourless needles, m. p. 95°, has the normal molecular weight in freezing benzene, gives a violet coloration with a little ferric chloride and an intense azure coloration with excess of the reagent, and readily reduces Fehling's solution, &c. T. H. P.

Bimolecular Nitriles. ERNST VON MEYER (*Chem. Zentr.*, 1908, ii, 591—594; from *Ber. K. Sächs. Ges. Wiss.*, *Math.-phys. Kl.*, 1908, **60**, 146—174. Compare Abstr., 1895, i, 582—585).—The author has further investigated the behaviour of the so-called dinitriles which have long been shown (*loc. cit.*) to react as two tautomeric forms; diacetonitrile, for instance, either as iminoethylacetonitrile or β-aminocrotononitrile,



$$\begin{array}{l}Me\cdot C{:}NH\\ \quad |\\ CH_2\cdot CN\end{array}$$

or



$$\begin{array}{l}Me\cdot C-NH_2\\ \quad ||\\ CH\cdot CN\end{array}.$$

[With W. SCHUMACHER.]—*Action of Arylamines on Diacetonitrile.*—Aniline gives the compound N-*phenyldiacetonitrile*,

$$NPh{:}CMe\cdot CH_2\cdot CN,$$

which crystallises in white needles, m. p. 115°; when treated with diazobenzene nitrate in pyridine solution, a *phenylhydrazone*, $NPh{:}CMe\cdot C({:}N\cdot NHPh)\cdot CN$, is formed, crystallising in greenish-yellow leaflets, m. p. 149°, and this, when treated with hydrogen chloride, gives phenylhydrazocyanoacetone. *N*-o-*Tolyldiacetonitrile*,

$$C_6H_4Me\cdot N{:}CMe\cdot CH_2\cdot CN,$$

is prepared in a similar manner, and crystallises in leaflets, m. p. 73°. *N*-m-*Tolyldiacetonitrile*, white, prismatic needles, m. p. 109°. *N*-p-*Tolyldiacetonitrile*, white needles, m. p. 102°. *N*-*Benzyldiacetonitrile*, white needles, m. p. 79°. a-*Naphthyldiacetonitrile*,

$$C_{10}H_7\cdot N{:}CMe\cdot CH_2\cdot CN,$$

prepared from diacetonitrile and α-naphthylamine, crystallises in leaflets, m. p. 112°. *β-Naphthyldiacetonitrile*, brown leaflets, m. p. 172°. The three isomeric mononitroanilines and *o*-chloroaniline do not react with diacetonitrile, but *N*-m-*chlorophenyldiacetonitrile*,

$$C_6H_4Cl\cdot N{:}CMe\cdot CH_2\cdot CN,$$

was readily obtained as white needles, m. p. 136°, and *N*-p-*chlorophenyldiacetonitrile* as white leaflets, m. p. 114°. With the three phenylenediamines, the following compounds have been obtained: o-*phenylenebisdiacetonitrile*, $C_6H_4(N{:}CMe\cdot CH_2\cdot CN)_2$, prismatic leaflets, m. p. 136°; m-*phenylenebisdiacetonitrile*, prisms, m. p. 185°; p-*phenylenebisdiacetonitrile*, square leaflets, m. p. 222°. p-*Hydroxyphenyldiacetonitrile*, $OH\cdot C_6H_4{:}N\cdot CMe\cdot CH_2\cdot CN$, crystallises in brown needles, m. p. 120°; p-*ethoxyphenyldiacetonitrile*, white needles, m. p. 138°. No combination takes place with *o*-aminobenzoic acid, but the other isomerides react, giving m-*carboxyphenyldiacetonitrile*,

$$CO_2H\cdot C_6H_4\cdot N{:}CMe\cdot CH_2\cdot CN,$$

white, prismatic needles, m. p. 206°; p-*carboxyphenyldiacetonitrile*, needle-shaped crystals, m. p. 158°. All the above-mentioned compounds are decomposed by hydrogen chloride into acetic acid, ammonia, and arylamine.

[With H. LEHMANN.]—*Action of Hydrazine Derivatives on Diacetonitrile.*—*Carbamidodiacetonitrile*, $NH_2\cdot CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CN$, is produced from diacetonitrile and semicarbazide hydrochloride; it forms small, white plates, m. p. 165°, which re-melt at 220°; an isomeric modification crystallising in prisms, m. p. 134°, has been observed. *Thiocarbamidodiacetonitrile*, $NH_2\cdot CS\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CN$, long needles, m. p. 106°. With thiosemicarbazide hydrochloride an isomeric form is obtained which crystallises in rhombic plates, m. p. 132°, re-melting at 162°. *Benzoylaminodiacetonitrile*, $COPh\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CN$, leaflets, m. p. 90°.

[With M. KLEINSTÜCK.]—*Action of Aldehydes on Dinitriles* (compare Mohr, Abstr., 1898, i, 26).—2 : 6-*Dimethyl*-3 : 5-*dihydropyridine*, prepared from diacetonitrile and formaldehyde, crystallises in yellow tablets, m. p. 222°, which are oxidised by nitric acid to 3 : 5-*dicyano*-2 : 6-*dimethylpyridine*, slender, white needles, m. p. 112°. Diacetonitrile with acetaldehyde (or paraldehyde) in presence of hydrogen chloride yields 3 : 5-*dicyano*-2 : 4 : 6-*trimethyldihydropyridine*, needle-shaped crystals, m. p. 170°, which also becomes oxidised by nitric acid to 3 : 5-*dicyano*-2 : 4 : 6-*trimethylpyridine*, m. p. 111°. Benzodiacetonitrile and benzaldehyde (or hydrobenzamide) react in presence of hydrogen chloride, forming 3 : 5-*dicyano*-2 : 4 : 6-*triphenyldihydropyridine*, small, yellow plates, m. p. 268°; when treated with nitric acid, 3 : 5-*dicyano*-2 : 4 : 6-*triphenylpyridine* is formed, which crystallises in needles, m. p. 238°. In a similar manner, 3 : 5-*dicyano*-2 : 6-*diphenyl*-4-o-*nitrophenyldihydropyridine* is produced from *o*-nitrobenzaldehyde; it forms small, yellow plates, m. p. 258°. From benzodiacetonitrile and hexamethyleneamine, 3 : 5-*dicyano*-2 : 6-*diphenyldihydropyridine* is obtained as small, yellow needles, m. p. 228°. With acetaldehyde or paraldehyde, 3 : 5-*dicyano*-2 : 6-*diphenyl*-4-*methyldihydropyridine* is obtained, needles, m. p. 267°.

[With W. HENNING.]—*Condensation of Diacetonitrile* (compare

Holtzwart, Abstr., 1889, 577).—The substance $C_8H_9N_3$, obtained from diacetonitrile by withdrawal of ammonia, is found to be 6-*amino*-3-*cyano*-2 : 4-*dimethylpyridine*, white needles, m. p. 222°, which, when treated with nitric acid, give 3-*cyano*-6-*hydroxy*-2 : 4-*dimethylpyridine*, needles, which melt above 260° (decomp.). The last-named substance gives, with phosphorus pentachloride, 6-*chloro*-3-*cyano*-2 : 4-*dimethylpyridine*, crystallising in thin leaflets, m. p. 65°; when boiled with methyl alcohol and sodium methoxide, 3-*cyano*-6-*methoxy*-2 : 4-*dimethylpyridine* is formed, needles, m. p. 96°, b. p. about 239°. This substance, when heated at 300°, changes to 3-*cyano*-1 : 2 : 4-*trimethyl*-6-*pyridone*, needle-shaped crystals, m. p. 125°. The above-mentioned chloro-compound (m. p. 65°), when reduced by zinc and hydrogen chloride, yields 3-*cyano*-2 : 4-*dimethylpyridine*, which forms colourless, prismatic crystals, m. p. 53°, b. p. 108°/15 mm., b. p. 218°; $C_8H_8N_2,HCl$, m. p. 187°; $C_8H_8N_2,HAuCl_4$, m. p. 172°; $C_8H_8N_2,HCl,HgCl_2$, m. p. 178°; $C_8H_8N_2,C_6H_2(NO_2)_3OH$, yellow prisms, m. p. 161°. When heated at 180° with alcoholic potassium hydroxide, *lutidinamide* is produced, which crystallises in needles with ½ mol. H_2O, m. p. 191°; when heated with hydrogen chloride at 220°, 2 : 4-dimethylpyridine (αγ-lutidine) is formed; *hydrochloride*, $C_5H_3Me_2N,HCl$; *platinichloride*, orange-red crystals, m. p. 208°. Contrary to Moir (Trans., 1902, 81, 10), the compound $C_8H_8ON_2$, which is isomeric with 3-cyano-6-hydroxy-2 : 4-dimethylpyridine (Holtwart, *loc. cit.*), is shown to be probably *cyanodimethyl*-6-*pyridone*; it gives with phosphorus pentachloride a compound, $C_8H_6N_2$, which is probably 2 : 4-*dicyano*-1 : 3-*dimethyl*cyclo*butane*.

[With C. Irmscher.]—*Condensation of Dinitriles with β-Ketocarboxylic Esters and Unsaturated Ketones.*—Condensation is incomplete with ketonic esters. From diacetonitrile and ethyl acetoacetate in the presence of pyridine, there is obtained 3-*cyano*-2 : 6-*dimethyl*-4-*pyridone*, which crystallises in small, white needles, m. p. 280°. With benzodiacetonitrile in the presence of hydrogen chloride, the same ester gives 3-*cyano*-2-*phenyl*-6-*methyl*-4-*pyridone*, white leaflets, m. p. 244°. From unsaturated ketones and dinitriles, instead of dihydropyridine derivatives being produced, pyridine derivatives are obtained, owing to loss of two hydrogen atoms. Benzylideneacetophenone and diacetonitrile yield 3-*cyano*-4 : 6-*diphenyl*-2-*methylpyridine*, which crystallises in needles, m. p 116°; $(C_{19}H_{14}N_2)_2,H_2PtCl_6$, golden-yellow leaflets. When heated with concentrated hydrochloric acid at 260°, it gives 4 : 6-*diphenyl*-2-*methylpyridine*-3-*carboxylic acid*, leaflets, m. p. 264°; the corresponding amide crystallises with 1 mol. H_2O, but the anhydrous substance, m. p. 216°. When the acid is distilled with soda-lime, 4 : 6-*diphenyl*-2-*methylpyridine* is produced, yellow needles, m. p. 156°. Potassium permanganate oxidises the acid compound to 4 : 6-*diphenylpyridine*-2 : 3-*dicarboxylic acid*, needles, m. p. 185° (decomp.). Diacetonitrile and anisylideneacetophenone with sodium ethoxide yield 3-*cyano*-4-p-*methoxyphenylphenyl*-6 : 2-*methylpyridine*, white needles, m. p. 157°. With piperonalacetophenone, 3-*cyano*-6-*phenyl*-4-*methylenedioxyphenyl*-2-*methylpyridine*, long, white needles, m. p. 238°; phenyl-*p*-tolylpropenone gives 3-*cyano*-4-*phenyl*-6-p-*tolyl*-2-*methylpyridine*, needles, m. p. 165°. Benzodiacetonitrile gives

3-*cyano*-2 : 4 : 6-*triphenylpyridine*, crystallising in needles, m. p. 220°; *p*-toludiacetonitrile gives 3-*cyano*-4 : 6-*diphenyl*-2-p-*tolylpyridine*, needles, m. p. 185°. From anisylideneacetophenone and benzodiacetonitrile there is obtained: 3-*cyano*-2 : 6-*diphenyl*-4-p-*methoxyphenylpyridine*, needles, m. p. 181°; and from anisylideneacetophenone and *p*-toludiacetonitrile, 3-*cyano*-6-*phenyl*-4-p-*methoxyphenyl*-2-p-*tolylpyridine*, needle-shaped crystals, m. p. 195°. Piperonalacetophenone yields 3-*cyano*-2 : 6-*diphenyl*-4-*methylenedioxyphenylpyridine*, m. p. 233°; 3-*cyano*-6-*phenyl*-2-p-*tolyl*-4-*methylenedioxyphenylpyridine* crystallises in needles, m. p. 245°. From cinnamylideneacetophenone, 3-*cyano*-2 : 6-*diphenyl*-4-*cinnamylpyridine*, needles, m. p. 184°; 3-*cyano*-6-*phenyl*-2-p-*tolyl*-4-*cinnamylpyridine*, needles, m. p. 181°. Benzylideneacetone, benzylidenecamphor, and benzylidenepyrazolone react in a different manner to benzylideneacetophenone.

[With W. SCHUMACHER.]—*Triazole Derivatives from Dinitriles.*—Diacetonitrile condenses with phenylazoimide, forming 1-*phenyl*-5-*methyltriazole*-4-*carboxylic acid*, which crystallises with $\frac{1}{2}H_2O$, m. p. 111°; the anhydrous substance has m. p. 146°. Benzodiacetonitrile gives 4-*cyano*-1 : 5-*diphenyltriazole*, crystallising in nearly white needles, m. p 242°, together with 1 : 5-*diphenyltriazole*-4-*carboxylamide*, yellow leaflets, m. p. 173°. J. V. E.

Action of Methyl Iodide on 2:6-Substituted Pyridinecarboxylic Acids.

RICHARD TURNAU (*Monatsh.*, 1908, **29**, 845—852).—An extension of the author's previous work on abnormal salts of betaines and pyridinecarboxylic acids (Abstr., 1905, i, 546).

2-Methylpyridine-6-carboxylic acid yields a basic *hydriodide*, $HI,C_5NH_3Me\cdot CO\cdot O\cdot C_5NH_4Me\cdot CO_2H$, which crystallises from alcohol in long needles and from water in stout prisms, turning brown above 200°, and decomposing at 230°; the same salt is also produced by the interaction of methyl iodide and the anhydrous acid. When shaken with silver chloride, the hydriodide yields 2-methylpyridine-6-carboxylic acid and the normal hydrochloride, m. p. 201° (decomp.) (Pinner and Lewin, Abstr., 1900, i, 409, give 138°).

2-*Methylpyridine*-6-*carboxylic chloride*, prepared by the action of thionyl chloride on the acid, forms slender, white needles, m. p. 195° (decomp.).

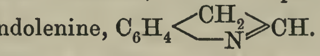
Quinoline-2-carboxylic acid does not react with methyl iodide at 100°, either with or without the presence of methyl alcohol. Pyridine-2 : 6-dicarboxylic acid does not react with methyl iodide at 100°, but in methyl-alcoholic solution gives the dimethyl ester. The author was unable to obtain a methiodide of 2-phenylcinchonic acid as described by Claus and Büttner (Abstr., 1893, i, 731).

Nicotinic acid hydriodide is almost colourless and rather unstable; iso*nicotinic acid hydriodide* forms slender, yellow needles, turning brown at 180°, and decomposing above 200°; both these are normal salts. J. C. C.

Electrolytic Reduction of the Indoles.

ORESTE CARRASCO (*Gazzetta*, 1908, **38**, ii, 301—308).—Tetrahydrocarbazole, 2 : 3-dimethylindole, 2-methylindole, and 1-methylindole can be completely reduced electrolytically in an acid solution by means of lead electrodes separated by a porous diaphragm, but indole itself, although largely reduced to the corresponding indoline, undergoes secondary condensations or polymerisations apparently analogous to those occurring during the reduction of quinoline (compare Ahrens, Abstr., 1897, i, 368).

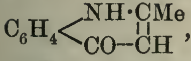
Thus tetrahydrocarbazole yields the carbazoline obtained by Graebe and Glaser (this Journ., 1872, 302); 2 : 3-dimethylindole gives 2 : 3-dimethylindoline, the *oxalate* of which, $C_{10}H_{13}N,H_2C_2O_4$, m. p. 134°, was prepared; 2-methylindole yields 2-methylindoline; 1-methylindole, 1-methylindoline, and indole, indoline. In the last case, a solid basic substance is also obtained, which is probably a polymeride of the hypothetical indolenine,



$C_6H_4<\overset{CH_2}{\underset{N}{}}>CH$.

The electrolytic reducing action is related to the number and position of the alkyl groups in the pyrrole nucleus. Thus 2 : 3-methylindole is reduced more easily than 2-methylindole, and the latter more easily than 1-methylindole, further proof being so afforded of the great stability of the 1-indole derivatives compared with the 2- or 3-derivatives. T. H. P.

Reduction of Nitro-compounds with Zinc Dust and Acetic Acid. II. Gustav Heller and Apostolos Sourlis (*Ber.*, 1908, **41**, 2692—2703. Compare this vol., i, 867).—When *o*-nitrophenylhydroxyethyl methyl ketone is reduced with zinc dust and 33% acetic acid in the cold, it yields 4-*keto*-2-*methyl*-1 : 4-*dihydroquinoline*,



$C_6H_4<\begin{matrix}NH\cdot CMe\\ CO-CH\end{matrix}$, which crystallises from water in long, colourless, hydrated needles, m. p. 77—78°. After remaining over sulphuric acid, it loses all but $\frac{1}{2}H_2O$. 2-Methylquinoline is formed on heating it with methyl sulphate. The *hydrochloride*,

$$C_{10}H_9ON,HCl,\tfrac{1}{2}H_2O,$$

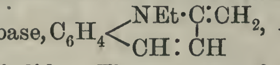
forms small, white rods, which darken at 190°, and decompose at 202°. The *hydriodide*, $C_{10}H_9ON,HI,\frac{1}{2}H_2O$, separates in long, cherry-red rods, m. p. 167°. The *zincichloride*, $(C_{10}H_9ON)_2HCl,ZnCl_2,H_2O$, has m. p. 211°. The *platinichloride*, $(C_{10}H_9ON)_4,H_2PtCl_6,2H_2O$, forms lemon-yellow prisms, m. p. 207° (decomp.). The *dichromate* occurs in small, orange-yellow rods, m. p. 133—134° (decomp.). The *picrate* crystallises in lemon-yellow, six-sided rhombohedra, m. p. 173°. When the base is treated with phosphoryl chloride and phosphorus pentachloride, 4-chloro-2-methylquinoline (Conrad and Limpach, Abstr., 1887, 680) is formed. This crystallises with $1H_2O$, which is lost in a desiccator. 4-*Keto*-1 : 4-*dihydroquinoline*-2-*carboxylic acid*, prepared by oxidising the base with potassium permanganate in alkaline solution, crystallises in colourless needles, m. p. 167° (decomp.); on reduction with hydriodic acid and red phosphorus, it yields quinoline-2-carboxylic acid. When 4-keto-2-methyl-1 : 4-dihydroquinoline is reduced with zinc dust and hydrochloric acid, it yields 2-methylquinoline, of which the following salts are described and some inaccurate statements concerning them in the literature corrected. The hydrochloride (mentioned by the author as not having previously been described, but referred to by

Doebner and von Miller, Abstr., 1883, 602), colourless needles, m. p. 224° (decomp.); the dichromate, yellow needles, m. p. 110°; the methiodide darkens at 230°, m. p. 234° (decomp.) (Doebner and von Miller, Abstr., 1884, 184, give 195°); the *zincichloride*, colourless rhombohedra, darkens at 205° and decomposes at 245°; this salt is formed in the reduction of *o*-nitrophenylhydroxyethyl methyl ketone, and if this process is carried on with addition of 1 part of hydrochloric acid, a yield of 52% of the theoretical amount of 2-methylquinoline is obtained. The mercurichloride of 2-methylquinoline has m. p. 184° (Pictet and Bunzl, Abstr., 1889, 971, give 165·5°), and the picrate, m. p. 194°.

2-*Methyldihydroquinoline*, prepared by reducing 2-methylquinoline with hydrochloric acid and zinc dust, forms feathery crystals, m. p. 178°, and is bimolecular. It differs from the 2-methyldihydroquinoline described by Doebner (Abstr., 1898, i, 385), and the termolecular compound prepared by Ahrens (Abstr., 1897, i, 370). The *picrate* forms small, dark brown rods, which sinter at 95° and decompose at 110°. J. C. C.

Constitution of Cyanine Dyes. EDUARD VONGERICHTEN and C. HÖFCHEN (*Ber.*, 1908, 41, 3054—3062. Compare Miethe and Book, Abstr., 1904, i, 622, 776).—The authors are in favour of Miethe and Book's constitutional formula for diethyl*iso*cyanine iodide (ethyl-red). Their support is based on the following considerations: (1) *Diethylchloro*iso*cyanine iodide*, obtained from the ethiodides of 6-chloroquinoline and 2-methylquinoline, has the formula $C_{23}H_{24}N_2ClI$. It crystallises from alcohol in a mixture of dark reddish-violet, flat needles, and of green crystals resembling ethyl-red, or from chloroform in homogeneous, green crystals. (2) Ethyl-red is a tertiary amine, since it forms a *methiodide*, $C_{24}H_{28}N_2I_2$, which crystallises in minute, brown needles, m. p. about 230°. It is decomposed by solution in alcohol, yielding ethyl-red. (3) In the condensation of the ethiodides of quinoline and 2-methylquinoline, the methyl group of the latter is concerned, as when two hydrogen atoms of this methyl group are replaced by the benzylidene group or by two methyl groups, the condensation with quinoline ethiodide does not take place.

The action of the alkali on the 2-methylquinoline ethiodide is supposed to give the ammonium hydroxide derivative, which is then transformed into the carbinol base, and this by loss of water gives the *iso*base,



$C_6H_4{<}\begin{matrix}NEt\cdot C{:}CH_2\\ CH{:}\overset{|}{C}H\end{matrix}$, which then condenses with the quinoline ethiodide. The presence of this grouping in ethyl-red is demonstrated by the formation of 1-ethyl-2-quinolone by the oxidation of ethyl-red, or its chloro-derivative with excess of cold potassium ferricyanide solution.

In the preparation of ethyl-red, the yield of dye is considerably lessened when more than two molecular proportions of potassium hydroxide are used for one of 2-methylquinoline methiodide and two of quinoline ethiodide.

6-Chloroquinoline *nitrate* forms colourless, glossy needles, m. p. 176°; the *chromate*, which can be used for purifying the base, golden-yellow needles, m. p. 168°, and the *ethiodide*, C_9H_6ClN,EtI, yellow plates, m. p. 168—169°.

*a-iso*Propylcinchoninic acid has m. p. 150°, not 146°, and *a-iso*propylquinoline methiodide, $C_{13}H_{16}NI$, m. p. 182°.

Ethyl-red is not formed when 2-methylquinoline ethiodide is added to a hot solution of quinoline ethiodide and alcoholic potash solution, but is formed when cold solutions are used. This indicates that 1-ethyl-2-quinolone and 1-ethyltetrahydroquinolone, which are formed by the action of hot alkali on the carbinol base, cannot be intermediate products in the formation of the dye.

Cold aqueous potassium hydroxide reacts with 2-methylquinoline ethiodide, yielding a base which is soluble in ether or benzene, and the base appears to be a carbinol base, as it yields 2-methylquinoline ethochloride and water when its dry benzene solution is treated with hydrogen chloride.

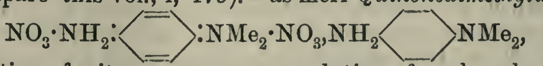
1-Methyl-4-quinaldone reacts with phosphorus pentachloride, yielding a crude product, which condenses with 2-methylquinoline ethiodide and alkali to ethyl-red. J. J. S.

Formation of 4-Oxycarbostyril from *o*-Nitrobenzoylacetic Acid. Kōichi Matsubara (*J. Coll. Sci. Tōkyō*, 1908, **25**, xvii, 1—3).—4-Oxycarbostyril (or 2 : 4-dihydroxyquinoline) is formed by adding an ammoniacal solution of *o*-nitrobenzoylacetic acid to an aqueous solution of ferrous sulphate to which an excess of ammonia has been added. W. H. G.

Action of Acid Esters on Quinoline Bases. Johann Spady (*Ber.*, 1908, **41**, 2902—2907).—On heating methyl salicylate with 2-methylquinoline at 180°, a quinaldine dye, $C_{22}H_{20}N_2$, phenol, and carbon dioxide are formed. The reaction is analogous to that between alkyl salicylates and primary or secondary amines studied by Tingle. The *dye* forms microscopic, yellow prisms from benzene, m. p. 190—191°; it dyes silk or cotton yarn similarly to quinaldine-yellow; it yields a sparingly soluble, crystalline hydrochloride and sulphate, and dissolves in concentrated sulphuric acid to a yellow solution having a bluish-green fluorescence.

Methyl salicylate reacts with quinoline at 150°, and energetically at 180—190°, forming a *compound*, $C_{20}H_{22}O_2N_2,\frac{1}{2}H_2O$, crystallising in minute, glistening, orange needles, which sinter at 281—282°, and melt and decompose at a higher temperature. It is soluble in water and alkaline hydroxides, and its solutions, particularly in alcohol or benzene, have a green fluorescence. E. F. A.

Quinonoid Compounds. XVII. *meri*-Quinoneimines. II. Richard Willstätter and Jean Piccard (*Ber.*, 1908, **41**, 3245—3252. Compare this vol., i, 475).—as-meri-*Quinonedimethyldiimonium nitrate*,



is prepared by the action of nitrous gases on a solution of *p*-phenylenedimethyldiamine in alcohol and nitric acid, cooled by a mixture of ice and calcium chloride. The leaflets are green by transmitted light, and show a copper metallic lustre; the solution is red.

Potassium ferricyanide in aqueous solution, when stirred into an acetic acid solution of the phenylenedimethyldiamine, forms green, rectangular plates of as-meri-*quinonedimethyldi-imonium ferricyanide*, $H_2Fe(CN)_6{\cdot}NMe_2{:}C_6H_4{:}NH,2NH_2{\cdot}C_6H_4{\cdot}NMe_2$.

Wurster and Schobig obtained a blue dye from tetramethylphenylenediamine which could only be analysed as the ferricyanide (Abstr., 1880, 111). Two *meri*-quinonoid compounds have been obtained by the authors, the blue salt, $C_{10}H_{16}N_2,H_3Fe(CN)_6$, and the new violet *salt*, $3C_{10}H_{16}N_2 + H_3Fe(CN)_6$ minus H_2.

From benzidine, two *meri*-quinonoid chromates have been obtained: the first, $NH{:}C_6H_4{:}C_6H_4{:}NH,4NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2,4H_2CrO_4$, is formed when a chromic acid solution is treated at 0° with an excess of an acetic acid solution of benzidine. It is blue, the other is brownish-violet, and is obtained when excess of chromic acid is employed. It has the composition:

$$NH{:}C_6H_4{:}C_6H_4{:}NH,3NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2,5H_2CrO_4$$

(compare Willstätter and Kalb, Abstr., 1906, i, 996).

The quinonoid derivatives of tetramethylbenzidine prepared by Willstätter and Kalb (Abstr., 1904, i, 1050) have been re-examined by the new titration method with stannous chloride. The formula of the yellow *holo*-quinonoid disulphate has been confirmed; the green *meri*-quinonoid dichloride has the constitution:

$$NMe_2Cl{:}C_6H_4{:}C_6H_4{:}NMe_2Cl,NMe_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NMe_2,6H_2O.$$

W. R.

Action of Halogens and Hydrogen Halides on Phenylhydrazine.

GEORG LOCKEMANN and E. WEINIGER (*Ber.*, 1908, 41, 3102—3108. Compare Fischer, this Journ., 1877, ii, 887; von Meyer, Abstr., 1887, 1042; Stollé, Abstr., 1903, ii, 100).—Iodine acts on phenylhydrazine dissolved in absolute ether, yielding pentaphenylhydrazine trihydriodide, iodobenzene, and nitrogen, thus:

$$6Ph{\cdot}N_2H_3 + 2I_2 = PhI + (Ph{\cdot}N_2H_3)_5,3HI + N_2.$$

Bromine acts in a similar manner, but chlorine yields only the normal hydrochloride.

Pentaphenylhydrazine trihydriodide, $(Ph{\cdot}N_2H_3)_5,3HI$, crystallises in thin, colourless leaflets, m. p. 137°. An alcoholic solution of the substance when treated with ether yields the *monohydriodide*,

$$Ph{\cdot}N_2H_3,HI,$$

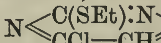
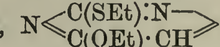
crystallising in colourless leaflets, m. p. 165°. The *basic* salt,

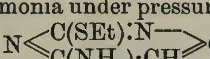
$$(Ph{\cdot}N_2H_3)_2,HI,$$

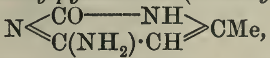
is prepared by passing small quantities of hydrogen iodide into an ethereal solution of phenylhydrazine; it crystallises in small, colourless needles, m. p. 132°.

Pentaphenylhydrazine trihydrobromide, $(Ph{\cdot}N_2H_3)_5,3HBr$, is obtained as a white, crystalline precipitate, m. p. 194—197°. Phenylhydrazine hydrobromide and the basic salt, $(Ph{\cdot}N_2H_3)_2,HBr$, melt at 218° and 183° respectively. These differ from the m. p.'s recorded by Le Canu (Abstr., 1903, i, 778), Broche (Abstr., 1894, i, 562), and Ponzio (Abstr., 1906, i, 482). W. H. G.

Action of Nitrous Esters on Hydrazine, Phenylhydrazine, and Benzylhydrazine in Alkaline Solution. Robert Stollé (*Ber.*, 1908, **41**, 2811—2813).—The author had already patented the same process as that since described by Thiele (this vol., ii, 940) for the preparation of azoimide. The best yields (80%) are obtained by boiling an alcoholic solution of hydrazine hydrate with amyl nitrite and sodium ethoxide. By neutralising hydrazine sulphate with aqueous potassium hydroxide and shaking the solution with alcohol, potassium hydroxide, and amyl nitrite, a 70% yield is obtained, and yields of 60% (of the hydrazine sulphate used) result when no alcohol is used. The author has also prepared *iso*diazobenzene salts by the action of ethyl nitrite on phenylhydrazine in presence of sodium or potassium ethoxide (compare Thiele, this vol., i, 927). The *silver* salt is white. Benzylhydrazine when treated with ethyl nitrite and sodium ethoxide in alcoholic solution yields, after some days, a mixture of sodium azoimide and sodium dibenzylhydrazine. J. C. C.

Pyrimidines. XXXVII. Synthesis of 4-Methylcytosine. Carl O. Johns (*Amer. Chem. J.*, 1908, **40**, 348—355).—Of the two methyl derivatives of cytosine having the methyl group attached to carbon, the 5-methyl compound has already been prepared (Wheeler and Johnson, Abstr., 1904, i, 624), and the 4-methyl compound is described in the present paper. When 6-oxy-2-ethylthiol-4-methylpyrimidine (obtained in an 80—90% yield by condensing ψ-ethylthiocarbamide hydrobromide with ethyl acetoacetate in aqueous sodium hydroxide) is heated with phosphoryl chloride, it is converted into 6-*chloro-2-ethylthiol-4-methylpyrimidine*,  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{C(SEt){:}N}\\ \mathrm{CCl{-}CH}\end{array}\!>\!\mathrm{CMe}$, b. p. 142°/15 mm., which, with sodium ethoxide, furnishes 6-*ethoxy-2-ethylthiol-4-methylpyrimidine*,  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{C(SEt){:}N{-}}\\ \mathrm{C(OEt){\cdot}CH}\end{array}\!>\!\mathrm{CMe}$, b. p. 154°/20 mm.

When 6-chloro-2-ethylthiol-4-methylpyrimidine is heated with alcoholic ammonia under pressure, it yields 6-*amino-2-ethylthiol-4-methylpyrimidine*,  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{C(SEt){:}N{-}}\\ \mathrm{C(NH_2){\cdot}CH}\end{array}\!>\!\mathrm{CMe}$, which forms crystals with a tetrahedral outline and a tendency to twinning, m. p. 115—116°. On evaporating this substance with concentrated hydrochloric acid, it gives 2-*oxy-6-amino-4-methylpyrimidine* (4-*methylcytosine*),



$$\mathrm{N}\!<\!\begin{array}{l}\mathrm{CO{-\!-\!-}NH}\\ \mathrm{C(NH_2){\cdot}CH}\end{array}\!>\!\mathrm{CMe},$$

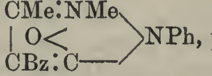
crystallising in anhydrous, slender, brittle prisms, which do not melt at 310°, but decompose slowly at higher temperatures. At 24°, 0·36 gram is dissolved by 100 c.c. of water. The *monohydrochloride* forms blunt, flat prisms with a hexagonal appearance; it sinters at 280°, and decomposes slowly above 300°. The basic *hydrochloride*,

$$(C_5H_7ON_3)_3,HCl,$$

forms pearly scales, which do not melt at 310°. The *nitrate*, clusters of blunt prisms, the *sulphate*, $(C_5H_7ON_3)_2,H_2SO_4,H_2O$, large, flat prisms, and the *picrate*, yellow needles, decomposing above 265°, are also described. J. C. C.

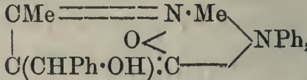
4-Keto-compounds of Pyrines. August Michaelis and F. Engelhardt (*Ber.*, 1908, **41**, 2668—2676).—The authors have prepared keto-compounds of the pyrines by a similar method to that used for the preparation of the azo-derivatives of antipyrine and thiopyrine (Michaelis and Schlecht, Abstr., 1906, i, 614), namely, by treating the corresponding ketopyrazolones or their chloropyrazoles with methyl sulphate. In the present paper, the 4-benzoyl derivatives of the pyrines are described.

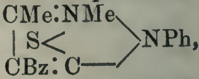
4-Benzoyl-1-phenyl-3-methyl-5-pyrazolone is best prepared by converting 1-phenyl-3-methyl-5-pyrazolone into the 5-benzoyl derivative, transforming the recrystallised substance into the 4:5-dibenzoyl derivative, and heating this with alcoholic potash according to Nef's method (Abstr., 1892, 146). Nef (*loc. cit.*) describes 4-benzoyl-1-phenyl-3-methylpyrazolone as forming yellow needles, m. p. 86°, and Knorr (Abstr., 1895, i, 396) gives m. p. 116—117°. The authors find that it exists in two isomeric modifications; the one separates from a mixture of light petroleum and chloroform in large, yellow, quadratic columns, m. p. 86°, and the other crystallises from alcohol in asbestos-like, white needles, m. p. 118°.

4-*Benzoylantipyrine*, 
$\begin{array}{l}\text{CMe:NMe}\\ |\ \text{O}<\qquad>\text{NPh}\\ \text{CBz:C}\end{array}$
, prepared from 4-benzoyl-1-phenyl-3-methylpyrazolone and methyl sulphate, forms colourless, rhombic columns, m. p. 148°. Its aqueous solution gives a red coloration with ferric chloride. The *hydrochloride* crystallises in hexagonal tablets, m. p. 218°. The *phenylhydrazone*, $C_{11}H_{11}ON_2{\cdot}CPh{:}N{\cdot}NHPh$, forms quadratic columns, m. p. 160°. The *hydrazone*,

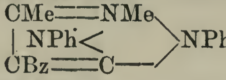
$$C_{11}H_{11}ON_2{\cdot}CPh{:}N{\cdot}NH_2,$$

crystallises in hexagonal prisms, m. p. 215°; with nitrobenzaldehyde it gives a yellow, insoluble *compound*, m. p. 350°; the *hydrochloride* of the hydrazone forms yellow, quadratic columns, m. p. 202°. The *oxime* of benzoylantipyrine, $C_{11}H_{11}ON_2{\cdot}CPh{:}N{\cdot}OH$, crystallises in long, hexagonal prisms, m. p. 197°.

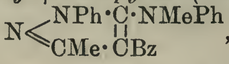
4-α-*Hydroxybenzylantipyrine*, 
$\begin{array}{l}\text{CMe}{=\!=\!=\!=}\text{N}{\cdot}\text{Me}\\ |\qquad\quad \text{O}<\qquad>\text{NPh}\\ \text{C(CHPh}{\cdot}\text{OH):C}\end{array}$
, prepared by reducing 4-benzoylantipyrine with sodium amalgam, crystallises in long, white, hexagonal prisms, m. p. 173°. It gives a strong antipyrine reaction with ferric chloride, and, on warming with dilute hydrochloric acid, furnishes benzylideneantipyrine hydrochloride (Knorr, Abstr., 1884, 1378), which is found to have the formula $C_{29}H_{28}O_2N_4,2HCl,7H_2O$. Benzoylantipyrine and α-hydroxybenzylantipyrine have no striking poisonous effects when administered to dogs.

5-*Chloro*-4-*benzoyl*-1-*phenyl*-3-*methylpyrazole methiodide*, prepared by treating the pyrazole (Michaelis and Bender, Abstr., 1903, i, 288) with methyl sulphate and subsequently adding potassium iodide to the aqueous solution, forms glistening, quadratic tablets, m. p. 166°. With sodium hydroxide, it yields 4-benzoylantipyrine, and with potassium hydrogen sulphide it gives 4-*benzoylthiopyrine*, 
$\begin{array}{l}\text{CMe:NMe}\\ |\ \text{S}<\qquad>\text{NPh}\\ \text{CBz:C}\end{array}$
, crystallising in flat, quadratic prisms, m. p. 217°. The *phenylhydr-*

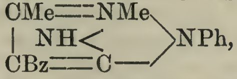
azone, $C_{11}H_{11}N_2S\cdot CPh\colon N\cdot NHPh$, crystallises in microscopic, yellowish-white needles, m. p. 280°, and the *methiodide* forms long, hexagonal prisms, m. p. 168°. When the latter is heated, it yields 4-benzoyl-ψ-thiopyrine (Michaelis and Lehmann, this vol., i, 691).

4-*Benzoylanilopyrine*,  prepared from 5-chloro-4-benzoyl-1-phenyl-3-methylpyrazole methiodide and aniline, forms dark yellow, rhombic tablets, m. p. 159°; the *phenylhydrazone*,

$C_{17}H_{16}H_3\cdot CPh\colon N\cdot NHPh$,

forms long, yellowish-white needles, m. p. 178°. The *methiodide* crystallises in large, colourless or pale rose-coloured, quadratic tablets, m. p. 172°, and, on heating, furnishes 4-*benzoyl*-ψ-*anilopyrine* (4-*benzoyl*-5-*methylanilino*-1-*phenyl*-3-*methylpyrazole*),  $N\begin{matrix}\diagup NPh\cdot C\cdot NMePh\\ \diagdown CMe\cdot CBz\end{matrix}$, which forms hexagonal columns, m. p. 144·5°.

The *methiodide* of 5-amino-4-benzoyl-1-phenyl-3-methylpyrazole (Michaelis and Bender, *loc. cit.*) crystallises in glistening, quadratic tablets, m. p. 238°. The *methochloride* forms glistening, white leaflets, and with aqueous sodium hydroxide gives 4-*benzoyliminopyrine* (2 : 5-*imino*-4-*benzoyl*-1-*phenyl*-2-*methyldihydropyrazole*),



which crystallises in small, yellow needles, m. p. 155°. J. C. C.

Piperazine Phosphates and Arsenates. A. Astruc and R. Brenta (*Bull. Soc. chim.*, 1908, [iv], 3, 963—966).—Piperazine forms with phosphoric acid the two salts: $C_4H_{10}N_2,H_3PO_4,H_2O$ and

$C_4H_{10}N_2,2H_3PO_4$.

Of these, both are acid to phenolphthalein, and the first is alkaline and the second neutral to helianthin. The potassium salt,

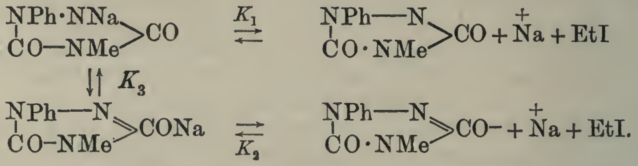
$C_4H_{10}N_2,KH_2PO_4$,

is neutral to phenolphthalein and alkaline to helianthin. The two arsenates are similar in constitution to the phosphates, and show like behaviour with the indicators named. The salts of the type

$C_4H_{10}N_2,H_3PO_4,H_2O$

may be regarded as analogous with disodium hydrogen phosphate or arsenate, and those of the type $C_4H_{10}N_2,2H_3PO_4$ may perhaps be regarded as salts of the acid, $2H_3PO_4$, mentioned by Giran (this vol., ii, 686). T. A. H.

Urazoles XIV. Reactions between Tautomeric Acids and Salts with Diazomethane and Alkyl Haloids. Salamon F. Acree, J. M. Johnson, R. F. Brunel, G. H. Shadinger, and Sidney Nirdlinger (*Ber.*, 1908, 41, 3199—3236. Compare this vol., ii, 163).—1-Phenylurazole and its derivatives are moderately strong acids, and yield salts not markedly hydrolysed, the dissociation constants of which are easily determined. They also react easily with alkyl halides, and as no slow tautomeric changes occur and the isomeric ethers so obtained are stable, these compounds are very suitable for an investigation of tautomeric phenomena. It has now been proved with practical certainty that both forms of the salts of 1-phenyl-4-methylurazole exist in solution, and that the alkyl halide reacts with the enolic as well as with the ketonic anion to form the O- and N-ethers.



$$\begin{array}{ccc} \begin{array}{l}\text{NPh·NNa}\\ \text{CO—NMe}\end{array}\!>\!\text{CO} & \overset{K_1}{\rightleftarrows} & \begin{array}{l}\text{NPh—N}\\ \text{CO·NMe}\end{array}\!>\!\text{CO}+\overset{+}{\text{Na}}+\text{EtI} \\ \downarrow\uparrow K_3 & & \\ \begin{array}{l}\text{NPh—N}\\ \text{CO—NMe}\end{array}\!>\!\text{CONa} & \underset{K_2}{\rightleftarrows} & \begin{array}{l}\text{NPh—N}\\ \text{CO·NMe}\end{array}\!>\!\text{CO}^{-}+\overset{+}{\text{Na}}+\text{EtI.} \end{array}$$

If K_3 is the alkylation constant, x the velocity of formation of the N-ether, and x' that of the O-ether, then

$$dx/dt = K(C_{\text{salt}} - x - x')(C_{\text{EtI}} - x - x');$$

$d(x+x')/dt = K + K'(C_{\text{salt}} - x - x')(C_{\text{EtI}} - x - x')$, and $K/K' = x/x' =$ N-ether/O-ether. The ratio between the quantities of the two stable alkyl or other derivatives from tautomeric substances must be independent of the time, and the ratio between the quantity of ethers and the alkylating reagent is dependent on three factors: (1) the relative reactivities of the tautomeric isomerides with the reagent; (2) the ratio of the isomerides if these exist in equilibrium, and (3) the velocity of transformation of one isomeride into the other as soon as the equilibrium is disturbed.

The hypotheses of Comstock, Wheeler, and Nef are discussed from this point of view, and considered to be erroneous. The theory (*loc. cit.*) has been confirmed and extended to all tautomeric phenomena. It would appear that the equilibrium is established between the molecules of the salt, and not the anions, as the addition of sodium iodide to solutions of ethyl iodide and sodium urazole does not cause a catalytic alteration in the ratio of O-ether to N-ether, although the nature of the urazole salt has a large effect. Thus ethyl iodide gives with the sodium, potassium, barium, and zinc salts of 1-phenyl-4-methylurazole in a $0{\cdot}3N$ solution in 40% alcohol at 60°, velocity constants: 0·42, 0·36, 0·28, and 0·05. The sodium salt of 1-phenyl-2-methylurazole yields with methyl iodide, 98% of the N-ether and 2% of the O-ether, whereas the silver salt gives a 50% yield of both. Experiments are quoted to show that by using the potassium and silver salts of 1-phenyl-4-methylurazole with ethyl iodide at 22°, 60°, and 90°, constant values of the ratio of two ethers are obtained; thus indicating that the equilibrium in solution is not markedly affected by temperature.

The effect of solvent has also been studied; thus the silver salt with ethyl iodide at 60° gives the ratio of the two ethers: in 40% alcohol, 40 : 60; in absolute alcohol, 33 : 67; in acetone, 39·5 : 60·5; in water, 37 : 63, and in ether, 35 : 65.

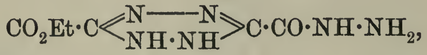
When different alkyl iodides are employed, this ratio of N- to O-ether is altered. The silver salt of 1-phenyl-2-methylurazole reacts quickly with methyl iodide to form 50% of each, and with ethyl iodide only slowly to give 90% O- and 10% N-ether.

Concentration has practically no effect; thus the sodium salt of

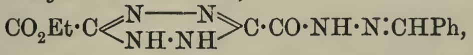
1-phenyl-4-methylurazole with ethyl iodide in 0·3, 0·15, 0·1, and 0·075*N* solutions gave the ratio 94 N- : 6 O-ether. W. R.

Action of Hydrazine Hydrate on Ethyl Bisdiazoacetate. Theodor Curtius and Eugen Rimele (*Ber.*, 1908, **41**, 3108—3116).—In continuation of the investigation of Curtius, Darapsky, and Bockmühl (this vol., i, 144), the behaviour of ethyl bisdiazoacetate towards hydrazine has been studied. It is found that the carbethoxy-groups of ethyl bisdiazoacetate are attacked by hydrazine hydrate, the first compound formed being ethyl bisdiazoacetate hydrazide, which is acted on by further quantities of hydrazine, yielding bisdiazoacetic acid dihydrazide. In this respect, ethyl bisdiazoacetate behaves like ethyl terephthalate; in both compounds, the carbethoxy-groups occupy 1 : 4-positions.

Ethyl bisdiazoacetate hydrazide is converted by nitrous acid into ethyl tetrazinedicarboxylate azoimide, and the dihydrazide into tetrazinedicarboxylic acid diazoimide. Ethyl bisdiazoacetate is most readily prepared by the action of diazomethane on an ethereal solution of bisdiazoacetic acid.



Ethyl bisdiazoacetate hydrazide, $\mathrm{CO_2Et{\cdot}C}\Big\langle\begin{matrix}\mathrm{N{-\!-\!-}N}\\ \mathrm{NH{\cdot}NH}\end{matrix}\Big\rangle\mathrm{C{\cdot}CO{\cdot}NH{\cdot}NH_2}$, prepared by the action of hydrazine hydrate on ethyl bisdiazoacetate in alcoholic solution, crystallises in small, soft, pale yellow needles, m. p. 228—231° (decomp.); the *hydrochloride*, $C_6H_{10}O_3N_6,HCl$, crystallises in slender, golden-yellow needles, m. p. 212°. The corresponding *methyl* ester, $C_5H_8O_2N_6$, has m. p. 211°. The following derivatives of the ethyl ester are prepared by shaking its solution in dilute hydrochloric acid with the aldehyde or by heating the hydrazide with the ketone: the *benzylidene* derivative,

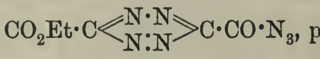


$$\mathrm{CO_2Et{\cdot}C}\Big\langle\begin{matrix}\mathrm{N{-\!-\!-}N}\\ \mathrm{NH{\cdot}NH}\end{matrix}\Big\rangle\mathrm{C{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh},$$

is obtained as a yellow, crystalline powder, decomposing at 233—234°; the p-*methoxybenzylidene* derivative, $C_{14}H_{16}O_3N_6$, sinters and melts at 237°; the *propylidene* derivative, $CO_2Et{\cdot}C_2H_2N_4{\cdot}CO{\cdot}NH{\cdot}N{:}CMe_2$, crystallises in slender, pale yellow needles, m. p. 115°; the *a-phenylethylidene* derivative, $C_{14}H_{16}O_3N_6$, crystallises in small, glistening, pale yellow needles, m. p. 182—185°; the *acetyl* derivative,

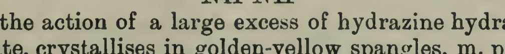
$$CO_2Et{\cdot}C_2H_2N_4{\cdot}CO{\cdot}NH{\cdot}NHAc,$$

prepared by acting on the hydrazide with acetic anhydride, forms a yellow powder, m. p. 166°.



Ethyl tetrazinedicarboxylate azoimide, $\mathrm{CO_2Et{\cdot}C}\Big\langle\begin{matrix}\mathrm{N{\cdot}N}\\ \mathrm{N{:}N}\end{matrix}\Big\rangle\mathrm{C{\cdot}CO{\cdot}N_3}$, prepared by treating a solution of the hydrazide hydrochloride with sodium nitrite, crystallises in violet-red leaflets, decomposes when heated, and liberates 2 mols. of nitrogen when its alcoholic solution is boiled.

Bisdiazoacetic acid dihydrazide,



$$\mathrm{NH_2{\cdot}NH{\cdot}CO{\cdot}C}\Big\langle\begin{matrix}\mathrm{N{-\!-\!-}N}\\ \mathrm{NH{\cdot}NH}\end{matrix}\Big\rangle\mathrm{C{\cdot}CO{\cdot}NH{\cdot}NH_2},$$

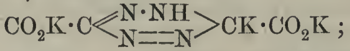
obtained by the action of a large excess of hydrazine hydrate on ethyl bisdiazoacetate, crystallises in golden-yellow spangles, m. p. 265—275°

(decomp.); the *hydrochloride*, $C_4H_8O_2N_8,2HCl$, and *dibenzylidene* derivative, $C_2H_2N_4(CO\cdot NH\cdot N{:}CHPh)_2$, a yellow powder, m. p. above 290°, were prepared and analysed.

Hydrazine bisdiazoacetate, $C_2H_2N_4(CO_2\cdot N_2H_5)_2$, prepared by adding hydrazine hydrate to an alcoholic solution of bisdiazoacetic acid, crystallises in small, yellow needles, m. p. 183—188°. *Ammonium hydrogen bisdiazoacetate*, $CO_2H\cdot C_2H_2N_4\cdot CO_2NH_4$, prepared by adding the acid (1 mol.) to the neutral ammonium salt (1 mol.), crystallises in orange-red needles, m. p. 192°. In the same way are obtained: *sodium hydrogen bisdiazoacetate*, $C_4H_3O_4N_4Na,H_2O$, yellow needles, and *potassium hydrogen bisdiazoacetate*, $C_4H_3O_4N_4K$. *Barium bisdiazoacetate*, $C_4H_2O_4N_4Ba,2H_2O$, is obtained as a yellow precipitate by adding barium chloride to an alcoholic solution of the acid. Attempts to prepare acid barium and silver salts were unsuccessful.

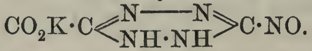
W. H. G.

ψ-Diazoacetic Acid. ERNST MÜLLER (*Ber.*, 1908, **41**, 3116—3139).—A continuation of the investigations by Curtius, Darapsky, and Müller (compare Abstr., 1906, i, 939; 1907, i, 21, 262, 359, 450, 451). When ethyl diazoacetate is treated with a concentrated aqueous solution of potassium hydroxide, it is converted into a tripotassium salt of ψ-diazoacetic acid,



$$CO_2K\cdot C\Big<\begin{matrix}N\cdot NH\\ N{=}N\end{matrix}\Big>CK\cdot CO_2K\,;$$

the formation of this salt is greatly accelerated by the presence of ethyl alcohol. It is converted by dilute acetic acid into the dipotassium salt, $CO_2K\cdot C\Big<\begin{matrix}N\cdot NH\\ N{=}N\end{matrix}\Big>CH\cdot CO_2K$, which, with glacial acetic acid, yields the potassium hydrogen salt, $CO_2K\cdot C\Big<\begin{matrix}N\cdot NH\\ N{=}N\end{matrix}\Big>CH\cdot CO_2H$. That the latter has this constitution follows from the fact that it yields a nitroso-derivative which undoubtedly has the constitution



$$CO_2K\cdot C\Big<\begin{matrix}N{-\!-}N\\ NH\cdot NH\end{matrix}\Big>C\cdot NO.$$

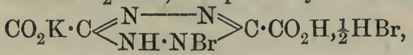
Potassium ψ-diazoacetate is hydrolysed by boiling acids, yielding glyoxylic acid (2 mols.), hydrazine (1 mol.), and nitrogen (1 mol.).

ψ-Diazoacetic acid has not yet been isolated, but an aqueous solution of the acid is obtained by treating the lead salt with hydrogen sulphide; the yellow solution thus obtained has a decided acid reaction, and gives the reaction characteristic of the ψ-series, namely, evolution of nitrogen and formation of hydrazine and glyoxylic acid when warmed with acids.

Unlike ψ-diazoacetamide, which is readily converted by a warm solution of potassium hydroxide into bisdiazoacetamide (compare Abstr., 1906, i, 939), potassium ψ-diazoacetate is converted only with difficulty into potassium bisdiazoacetate. The formation of potassium bisdiazoacetate from potassium diazoacetate observed by Hantzsch and Lehmann (Abstr., 1901, i, 678) must therefore take place through the intermediate ψ-diazoacetate.

An aqueous solution of potassium ψ-diazoacetate is converted by bromine into potassium hydrogen bromodihydrotetrazinedicarboxylate;

it is always obtained with $\frac{1}{2}$HBr, and probably has the formula



$$CO_2K\cdot C{<}\begin{matrix}N\text{———}N\\ NH\cdot NBr\end{matrix}{>}C\cdot CO_2H,\tfrac{1}{2}HBr,$$

since it is also formed by the action of bromine on potassium bisdiazoacetate, and is reduced by hydrogen sulphide to bisdiazoacetic acid. All attempts to remove the $\frac{1}{2}$HBr lead to the decomposition of the substance; thus it is converted by an aqueous solution of potassium acetate into potassium tetrazinedicarboxylate, and by sulphurous acid into tetrazinecarboxylic acid.

Tripotassium ψ-diazoacetate, $C_4HO_4N_4K_3,2H_2O$, is obtained as a pale yellow precipitate, which becomes brownish-yellow when exposed to light; the *dipotassium* salt, $C_4H_2O_4N_4K_2,H_2O$, as a lemon-yellow precipitate; the *potassium hydrogen* salt, $C_4H_3O_4N_4K,H_2O$, as a bright yellow precipitate; the *silver* salt, $C_4HO_4N_4Ag_3$, and *lead* salt,

$$C_8H_2O_8N_8Pb_3,$$

as yellow precipitates by adding silver nitrate or lead acetate to aqueous solutions of the dipotassium salt. *Dipotassium ammonium ψ-diazoacetate*, $C_4HO_4N_4K_2NH_4$, is obtained as hard, yellow leaflets by saturating a cold aqueous solution of the potassium salt with ammonia.

Potassium hydrogen bromodihydrotetrazinedicarboxylate,

$$C_4H_2O_4N_4BrK,\tfrac{1}{2}HBr,$$

forms a brick-red powder; it is converted by an aqueous solution of potassium acetate into *potassium tetrazinedicarboxylate*, $C_4O_4N_4K_2$, a violet-red precipitate, which yields with acetic acid the *salt*,

$$C_4HO_4N_4K,\tfrac{1}{2}Ac\cdot OH,$$

obtained as an orange powder; the latter loses acetic acid at 90°, yielding *potassium hydrogen tetrazinedicarboxylate*, $C_4HO_4N_4K$, a carmine-red powder.

Ethyl tetrazinedicarboxylate, $C_2N_4(CO_2Et)_2$, is prepared by the action of nitrous gases on an ethereal solution of ethyl bisdiazoacetate; it crystallises in long, purple prisms, m. p. 105—106° (decomp.).

Potassium nitrosodihydrotetrazinecarboxylate, $CO_2K\cdot C_2H_2N_4\cdot NO$, is obtained by adding acetic acid to an aqueous solution of potassium ψ-diazoacetate and nitrite as a bright yellow precipitate, m. p. 170° (decomp.). It is converted by hydrogen sulphide into a *sulphur dioxide additive* compound of *potassium* 1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*-3-*carboxylate*, obtained as a pale yellow, crystalline substance. A strong aqueous solution of this substance, when treated with sulphuric acid, yields 1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*-3-*carboxylic acid*,

$$C_2H_3N_4\cdot CO_2H,H_2O,$$

which crystallises in glistening, yellow scales, m. p. 93—105° (decomp.). When heated at 60—70° for forty-five minutes, it is converted into 1-amino-3 : 4-triazole (compare Bülow, Abstr., 1906, i, 905; 1907, i, 99). W. H. G.

So-called Ethyl *iso*Diazoacetate. THEODOR] CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1908, 41, 3140—3160).—Contrary to the statement of Hantzsch and Lehmann (Abstr., 1901, i, 678), the compound described by these authors as ethyl potassio*iso*diazoacetate, $\mathrm{CO_2Et\cdot C}<\begin{matrix}\mathrm{N}\\ |\\ \mathrm{NK}\end{matrix}$, when treated with dilute acid liberates nitrogen; the solution is then found to contain ethyl glyoxylate (2 mols.) and hydrazine (1 mol.). If the solution is boiled for some time, the ethyl glyoxylate is hydrolysed, and the glyoxylic acid reacts with the hydrazine, yielding ammonia and oxalic acid. It is therefore evident that the compound is not ethyl potassio*iso*diazoacetate, since this substance when hydrolysed would yield only ethyl oxalate and hydrazine. The compound prepared according to the directions of Hantzsch and Lehmann is shown to have the composition $\mathrm{CO_2Et\cdot C}<\begin{matrix}\mathrm{N\cdot NH}\\ \mathrm{N{=}N}\end{matrix}>\mathrm{CK\cdot CO_2Et,KOEt}$; that is, it is an *additive* product of *potassium ethoxide* with *potassium diethyl ψ-diazoacetate* (compare Müller, preceding abstract), which, when hydrolysed decomposes, thus: $\mathrm{C_2H_2N_4(CO_2Et)_2} \xrightarrow{2H_2O} \mathrm{2CO_2Et\cdot CHO + N_2H_4 + N_2}$. An aqueous solution of this substance, contrary to the statements of Hantzsch and Lehmann (*loc. cit.*), yields with silver nitrate the *silver* salt, $\mathrm{C_8H_{11}O_4N_4Ag,\frac{1}{2}Ag_2O}$, obtained as a greenish-black precipitate, and with mercuric chloride a dense, yellowish-brown precipitate of a complex *mercury* salt. The potassium salt is converted by an aqueous solution of potassium hydroxide (1 : 1) into potassium ψ-diazoacetate (compare Müller, *loc. cit.*).

Sodium diethyl ψ-diazoacetate, $\mathrm{CO_2Et\cdot C_2HN_4Na\cdot CO_2Et,NaOEt}$, described by Hantzsch and Lehmann as ethyl sodio*iso*diazoacetate, $\mathrm{CO_2Et\cdot CNaN_2,\frac{1}{2}H_2O}$, is best prepared by the action of sodium ethoxide, prepared by Brühl's method, on ethyl diazoacetate.

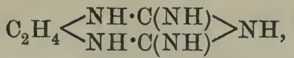
The substance which separates as an oil when an aqueous solution of either of the above salts is treated with dilute acids could not be purified, and all attempts to prepare derivatives were unsuccessful.

W. H. G.

Products of the Transformation of Ethyl Diazoacetate under the Influence of Alkalis. THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1908, **41**, 3161—3172).—A summary of the results obtained during the investigation on the behaviour of ethyl diazoacetate towards alkalis (compare Curtius, Darapsky, and Müller, Abstr., 1906, i, 939; 1907, i, 21, 262, 359, 450, 451, and preceding abstract; Müller, preceding abstract).

W. H. G.

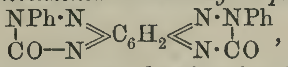
Ethylenediguanide. EMIL DITTLER (*Monatsh.*, 1908, **29**, 645—652).—Whilst monoamines form additive compounds (the monosubstituted diguanides) with dicyanodiamide, Ziegelbauer observed (Abstr., 1897, i, 142) that the action of *o*-phenylenediamine on dicyanodiamide leads to the formation of ammonia and *o*-phenylenediguanide, $\mathrm{C_6H_4}<\begin{matrix}\mathrm{NH\cdot C(NH)}\\ \mathrm{NH\cdot C(NH)}\end{matrix}>\mathrm{NH}$. With the object of determining if this formation of a disubstituted diguanide is a general reaction of diamines, the author has studied the action of ethylenediamine on dicyanodiamide, and has found that here, also, the reaction leads to the formation of ammonia and a disubstituted diguanide.

Ethylenediguanide,  $C_2H_4<\begin{matrix}NH\cdot C(NH)\\ NH\cdot C(NH)\end{matrix}>NH$, formed by the action of ethylenediamine on dicyanodiamide at 80—150°, is isolated as the *sulphate* of the copper derivative, $(C_4H_8N_5)_2Cu,H_2SO_4,3H_2O$, which separates in rose-red, microscopic needles, and dissolves sparingly in water, but readily in aqueous alkalis, forming red solutions. The *hydrogen sulphate*, $C_4H_9N_5,H_2SO_4$, forms hygroscopic, white needles, and gives characteristic reactions with nickel, cobalt, gold, and platinum salts, and with chromic, picric, and picrolonic acids. The *sulphate*, $(C_4H_9N_5)_2,H_2SO_4$, *hydrogen chloride*, $C_4H_9N_5,2HCl$, *chromate*, $(C_4H_9N_5)_2,H_2CrO_4$, and *picrolonate*, $C_4H_9N_5,C_{10}H_8O_5N_4$, are described. The free base, liberated from the sulphate by cold baryta water, is obtained as a syrup, which decomposes above 150°, yielding complicated products. The action of boiling baryta water on the sulphate, on the other hand, leads to the formation of ethylenediamine. G. Y.

Aromatic Monatomic Cyanamides. PAUL PIERRON (*Ann. Chim. Phys.*, 1908, [viii], **15**, 145—278).—Mainly a résumé of work already published (Abstr., 1905, i, 125; 1906, i, 772; 1907, i, 121); the following compounds are described for the first time: *ψ-cumylcyanamide*, $C_6H_2Me_3\cdot NH\cdot CN$, colourless prisms, m. p. 126°; the *carbamide* and the *benzoyl* derivatives melt at 237° and 94° respectively; p-*iodophenylcyanamide*, $C_6H_4I\cdot NH\cdot CN$, m. p. 110°, and the *carbamide*, m. p. 244°; *benzeneazo*-m-*ethoxycyananilide*, $CN\cdot NH\cdot C_6H_3(OEt)\cdot N\colon NPh$, m. p. 81—82°; and the following corrections in melting points are recorded: the benzoyl derivative of benzeneazo-*p*-cyananilide has m. p. 191°, and not 161°; benzeneazo-*m*-tolylcarbamide has m. p. 186°, and not 152°, and benzeneazo-*p*-cyano-*o*-ethoxyanilide has m. p. 120°, and not 121° (compare Abstr., 1906, i, 772).

With the view of preparing the corresponding dicyanamides and their derivatives, the author has examined the behaviour of the phenylenediamines with cyanogen bromide.

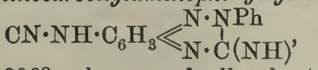
m-Phenylenediamine yields m-*phenylenedicyanamide*, $C_6H_4(NH\cdot CN)_2$, m. p. 205—207°. When heated rapidly, it condenses with diazobenzene chloride to yield the following products: (1) *benzeneazo*-m-*phenylenedicyanamide*, $C_6H_2(CN\cdot NH)_2(N\colon NPh)_2$, m. p. 250—252°; (2) m-*bis-keto-2-phenylbenzotriazine* (*dibenzeneazodicarbonyl*-m-*phenylenediamine*)



$$\begin{matrix}NPh\cdot N\\ |\\ CO—N\end{matrix}\!\!\gg C_6H_2 \ll\!\!\begin{matrix}N\cdot NPh\\ |\\ N\cdot CO\end{matrix},$$

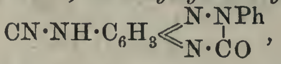
m. p. 310°; (3) *benzeneazo*-m-*phenylenedicarbamide*,

$$NPh\colon N\cdot C_6H_3(NH\cdot CO\cdot NH_2)_2,$$

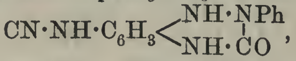
m. p. 238—240°; (4) *imino*-m-*cyanamido-2-phenylbenzotriazine* (*benzeneazoaminocarbonylaminophenylcyanamide*; *iminocarbonylcyanochrysoidine*),  $CN\cdot NH\cdot C_6H_3\ll\begin{matrix}N\cdot NPh\\ |\\ N\cdot C(NH)\end{matrix}$, m. p. 200° when heated rapidly, or 290° when gradually heated; the *hydrochloride* has m. p. 230°.

m-*Cyanaminophenylcarbamide*, $CN\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2$, m. p. 210°, has a pronounced sweet taste, and condenses with diazobenzene chloride to form *keto*-m-*cyanamido-2-phenylbenzotriazine* (*benzeneazo-*

carbonyl-m-*amidocyananilide* ; *carbonylcyanochrysoidine*),



$$CN\cdot NH\cdot C_6H_3\ll\begin{array}{l}N\cdot NPh\\ N\cdot CO\end{array},$$

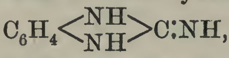
m. p. 258°; the corresponding *carbamide* has m. p. 300°, and, on reduction, it yields *keto*-m-*cyanamido-2-phenyldihydrobenzotriazine* (*dihydrocarbonylcyanochrysoidine*),  $CN\cdot NH\cdot C_6H_3<\begin{array}{l}NH\cdot NPh\\ NH\cdot CO\end{array}$, m. p. 210°.

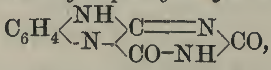
m-*Cyanoaminoacetanilide*, $CN\cdot NH\cdot C_6H_4\cdot NHAc$, m. p. 205—207°, condenses with diazobenzene chloride to form *benzeneazoacetamidocyananilide* (*acetylcyanochrysoidine*), $CN\cdot NH\cdot C_6H_3(NAc)\colon N\cdot NHPh$, m. p. 246° ; *cyanochrysoidine*, $CN\cdot NH\cdot C_6H_3(NH)\colon N\cdot NHPh$, has m. p. 186°, and the *benzoyl* derivative has m. p. 233°.

In the case of *p*-phenylenediamine, the dicyanamide derivative could not be isolated in the pure state ; p-*cyanaminophenylcarbamide*,

$$CN\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2,$$

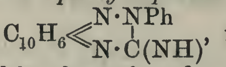
has m. p. 255°, and does not form a stable compound with diazobenzene chloride.

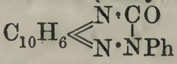
o-Phenylenediamine does not form cyanamide derivatives, but yields o-*phenyleneguanidine*,  $C_6H_4<\begin{array}{c}NH\\ NH\end{array}>C\colon NH$, m. p. 222°, when treated with cyanogen bromide ; the *benzoyl* derivative has m. p. 236° ; it is converted into *iminodicarbonyl*-o-*phenyleneguanidine*,



$$C_6H_4<\begin{array}{l}NH>C\!=\!=\!=\!N\\ -N-<CO-NH\end{array}>CO,$$

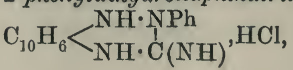
by the further action of cyanogen bromide, and the same compound is obtained by the action of cyanogen bromide on *o*-phenylenediamine in the presence of sodium hydrogen carbonate, or by the condensation of *o*-phenyleneguanidine with biuret.

β-Naphthylcyanamide condenses with diazobenzene chloride to form *imino-2-phenylnaphthatriazine* (*benzeneazoiminocarbonyl-β-naphthylamine*),  $C_{10}H_6\ll\begin{array}{l}N\cdot NPh\\ N\cdot C(NH)\end{array}$, m. p. 160°, and the same compound is obtained by the action of cyanogen bromide on benzeneazo-*β*-naphthylamine ; the *hydrochloride*, m. p. 230°, and the *dichromate* have been prepared. When the base is treated with acids, alkalis, or benzoyl chloride, it is converted into keto-2-phenylnaphthatriazine,



$$C_{10}H_6\ll\begin{array}{l}N\cdot CO\\ N\cdot NPh\end{array}$$

(compare Goldschmidt and Rosell, Abstr., 1890, 614 ; Busch, Abstr., 1900, i, 59), and, on reduction with stannous chloride, it yields the *hydrochloride* of *imino-2-phenyldihydronaphthatriazine*,



$$C_{10}H_6<\begin{array}{l}NH\cdot NPh\\ NH\cdot C(NH)\end{array},HCl,$$

m. p. 242—245°. M. A. W.

Azo-compounds of Salicylic Acid. Eugène Grandmougin and Julien Guisan (*Chem. Zentr.*, 1908, ii, 310—311 ; from *Rev. gén. Matières Colorantes*, 1908, 12, 129—137. Compare Abstr., 1907, i, 987).—When aminosalicylic acid and *p*-phenylenediamine are reduced by means of sodium hydrogen sulphite in hot aqueous solution, p-*nitrobenzeneazosalicylic acid*, m. p. 256°, is formed.

m-*Tolueneazosalicylic acid* is a yellow, crystalline substance, m. p. 208°; *acetyl* compound, m. p. 155°. p-*Tolueneazosalicylic acid* forms yellowish-brown needles, m. p. 214°; the sodium salt is known as flavazole, and the *acetyl* compound, $C_{16}H_{14}O_3N_2$. pale yellow crystals, m. p. 159·5°. m-*Nitrotolueneazosalicylic acid*, $C_{14}H_{11}O_5N_3$, prepared from diazotised *m*-nitro-*p*-toluidine and salicylic acid in alkaline solution, forms yellow needles, m. p. 242°; the *acetyl* compound, $C_{16}H_{13}O_6N_3$, large, yellow crystals, m. p. 171°.

o-*Nitrotolueneazosalicylic acid*, prepared in like manner, crystallises in brown needles, m. p. 210°, which, when reduced with hydrogen sulphite, form a *triazole* compound; the *acetyl* compound crystallises in brownish-yellow needles, m. p. 180°. p-*Acetylaminobenzeneazosalicylic acid*, $C_{15}H_{13}O_4N_3$, forms a brownish-yellow, crystalline powder, m. p. 245° (decomp.); the *diacetyl* compound, yellow needles, m. p. 200° (decomp.). When this is treated with strong sulphuric acid, p-*aminobenzeneazosalicylic acid*, $NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}CO_2H$, is produced, which forms a grey, crystalline powder, m. p. 230° (decomp.), and gives with carbonyl chloride the diaminodiphenyl derivative of carbamide, $CO[NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}CO_2H]$. p-*Hydroxybenzeneazosalicylic acid*, $C_{13}H_{10}O_4N_2$, prepared by the diazo-reaction from *p*-aminobenzeneazosalicylic acid, or from *p*-aminophenol and salicylic acid, or from aminosalicylic acid and phenol, crystallises in brown needles, m. p. 236°. p-*Ethoxybenzeneazosalicylic acid*, $C_{15}H_{14}O_4N_2$, prepared from diazotised phenetidine and salicylic acid, is a green, crystalline powder, m. p. 208°; the *acetyl* compound, yellow crystals, m. p. 158·5°. m-*Carboxybenzeneazosalicylic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}CO_2H,$$

prepared from *m*-aminobenzoic acid, has m. p. about 280° (decomp.). o-*Carboxybenzeneazosalicylic acid*, from anthranilic acid, forms yellow crystals, m. p. 219° (with sublimation). m-*Sulphobenzeneazosalicylic acid*, prepared from metanilic acid, gives a crystalline sodium salt of the composition $Na{\cdot}C_{13}H_9O_6N_2S,3H_2O$. When diazotised nitroaniline and diazotised 2-naphthylamine-7-sulphonic acid act on salicylic acid, some tris-azo-compound and phenol-bis-azo-compound are found together with the bis-azo-derivative. J. V. E.

Aromatic and Aliphatic *iso*Diazo-compounds (*iso*Azotates) from Hydrazines. JOHANNES THIELE (*Ber.*, 1908, **41**, 2806—2811).—When phenylhydrazine is treated with an alkyl nitrite and alkali, it is smoothly converted into the corresponding metallic salt of *iso*diazobenzene, nitrogen monoxide being formed at the same time. In the well-known production of diazonium salts from phenylhydrazine salts and nitrous acid and from nitrosophenylhydrazine, the author has been able to show that nitrogen monoxide is formed here also, and he considers that the process involves the intermediate formation of dinitrosohydrazines, $R{\cdot}N(NO){\cdot}NH{\cdot}NO$, or the alkali salts of their tautomerides. It is probable, also, that in the interation of hydrazine and nitrous acid (Dennstedt and Göhlich, Abstr., 1898, ii, 425), dinitrosohydrazine is formed, which, with the possible intermediate formation of a compound $N_3{\cdot}NO$, may decompose according to the equation: $NO{\cdot}NH{\cdot}NH{\cdot}NO = N_2O + N_2 + H_2O$. Further, azoimide and nitrous acid decompose, thus: $N_3H + HNO_2 = N_2 + N_2O + H_2O$, so that for each molecule of nitrogen monoxide formed in the above reaction one molecule of azoimide is lost.

Nitrosophenylhydrazine forms salts with bases, and, on heating its solutions in indifferent solvents, it decomposes into aniline and nitrogen monoxide; moreover, it does not form nitrosohydrazones with acetaldehyde or benzaldehyde, and it is suggested that its constitution may be represented as $C_6H_5{\cdot}NH{\cdot}NH{\cdot}NO$, or the tautomeric expression.

Nitrosobenzylhydrazine gives the first two reactions, but gives the normal hydrazone with benzaldehyde, so that the symmetrical formula $CH_2Ph{\cdot}NH{\cdot}NH{\cdot}NO$ cannot be assigned to it. Benzylhydrazine also gives the corresponding *iso*diazotate, and, as this may be regarded as belonging to the aliphatic series, it is termed *sodium benzyl*iso*azotate*, $C_6H_5{\cdot}CH_2{\cdot}N{:}N{\cdot}ONa$. This compound, which forms white needles, resembles sodium benzene*iso*diazotate in its reactions, except that it cannot be converted into a diazonium salt and does not yield azo-dyes; with acids, nitrogen is evolved.

Sodium benzene*iso*diazotate, prepared by adding ethyl nitrite mixed with ether to a cold mixture of phenylhydrazine, sodium methoxide, and ether, gives, in aqueous solution, with ferric chloride a brown, with copper sulphate a blackish-violet, and with mercuric nitrate a white, precipitate. Sodium *p*-nitrobenzene*iso*diazotate and sodium benzyl*iso*azotate give similar reactions.

An aqueous solution of nitrosophenylhydrazine gives with ferric chloride a transient violet coloration, with copper acetate a precipitate followed by reduction, and with mercuric nitrate a yellow precipitate sparingly soluble in dilute nitric acid. The *sodium* salt, $C_6H_5{\cdot}N_3HONa$, obtained by adding sodium methoxide to the ethereal solution, is white; with water, nitrosophenylhydrazine is regenerated.

Nitrosobenzylhydrazine gives with copper acetate a pale precipitate soluble in dilute acids, which reddens on warming. With mercuric nitrate, a yellow precipitate, soon turning white, is produced, which is sparingly soluble in nitric acid. The *sodium* salt, $C_7H_8N_3{\cdot}ONa$, resembles that of nitrosophenylhydrazine. J. C. C.

Hydrolysis of Legumelin from the Pea (Pisum sativum). THOMAS B. OSBORNE and FREDERICK W. HEYL (*J. Biol. Chem.*, 1908, 5, 197—206).—Legumelin is the albumin which occurs in many leguminous seeds. The following table compares the percentage of hydrolytic products in legumelin and leucosin, the albumin of wheat:

	Legumelin.	Leucosin.
Glycine	0·50	0·94
Alanine	0·92	4·45
Valine	0·69	0·18
Leucine	9·63	11·34
Proline	3·96	3·18
Phenylalanine	4·79	3·83
Aspartic acid	4·11	3·35
Glutamic acid	12·96	6·73
Tyrosine	1·56	3·34
Arginine	5·45	5·94
Histidine	2·27	2·83
Lysine	3·03	2·75
Ammonia	1·26	1·41
Total	51·15	50·53

Tryptophan is present in both; serine and cystine were not estimated. W. D. H.

Hydrolysis of Vicilin from the Pea (Pisum sativum). Thomas B. Osborne and Frederick W. Heyl (*J. Biol. Chem.*, 1908, 5, 187—196).—Vicilin is a globulin occurring in the pea, horse-bean, and lentil. It differs from legumin in containing more carbon, less nitrogen, and much less sulphur. It contains the smallest proportion of sulphur yet found in any protein (0·1—0·2%). The following table compares the percentage of hydrolytic products of the two proteins:

	Vicilin.	Legumin.
Glycine	0·0	0·38
Alanine	0·5	2·08
Valine	0·15	?
Leucine	9·38	8·00
Proline	4·06	3·22
Phenylalanine	3·82	3·75
Aspartic acid	5·30	5·30
Glutamic acid	21·34	16·97
Serine	?	0·53
Cystine	not determined	
Oxyproline	,,	,,
Tyrosine	2·38	1·55
Arginine	8·91	11·71
Histidine	2·17	1·69
Lysine	5·40	4·98
Ammonia	2·03	2·05
Tryptophan	present	present
Total	65·44	62·22

W. D. H.

Applicability of the Laws of Amphoteric Electrolytes to Serum Globulin. T. Brailsford Robertson (*J. Biol. Chem.*, 1908, 5, 155—162).—Polemical against H. Lundén (*ibid.*, 267).

W. D. H.

The Swelling of Fibrin. Martin H. Fischer (*Pflüger's Archiv*, 1908, 125, 99—110. Compare Abstr., 1907, i, 1095).—Fibrin swells more in acids than in distilled water; various acids produce this effect better than others; for instance, hydrochloric acid is the most and sulphuric acid the least effective of those investigated. The amount of swelling is dependent on the concentration of the acids. Alkalis also cause fibrin to swell in various degrees in proportion to the concentration. Beyond a certain point in the case both of acid and alkali, the swelling decreases. Alkalis produce more swelling than acids of the same strength. The addition of salts lessens the swelling, as also do non-electrolytes (urea, sugar, &c.). The taking up and giving out of water is a reversible phenomenon. W. D. H.

Solubility of Zein in Different Solvents. Gino Galeotti and G. Giampalmo (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 118—126).—Zein (a protein which occurs in maize) is insoluble in water and in alcohol, but is readily soluble in a mixture of them. The maximum solubility is observed with 60% alcohol. The solutions in alcohol stronger than 45% are clear and mobile, those in weaker alcohols are turbid and viscous. The addition of xylene, ether, or light petroleum does not precipitate zein from these solutions unless enough is added to form a second liquid phase. The solubility curve for mixtures of chloroform and 85% alcohol is found to possess two maxima, one about 16% and the other about 54% of chloroform. The solubility of zein in mixtures of water, alcohol, and acetone is very thoroughly studied, and the results represented by a diagram. The mixtures containing acetone dissolve less zein than the corresponding mixture of water and alcohol. The two series of solutions (clear and easily filtered—turbid and not readily filtered) are also found in the acetone mixtures. Zein is insoluble in all the pure solvents tried.

T. E.

Another Method of Measuring Large Molecular Masses. William Sutherland (*Phil. Mag.*, 1908, [vi], 16, 497—512).—From a relationship, previously deduced by the author, between the molecular conductivity, the concentration, the viscosities of the solvent and solution, the mass of the atom of hydrogen, the dielectric capacity of the solvent, and the dissociating force which causes complete ionisation, the author has deduced the molecular masses of globulin and casein. The globulin ions produced by hydrochloric acid in aqueous solutions are found to be bivalent, and their molecular mass about 10,000. The molecular mass of the casein ion is given as 2605. On the assumption that the casein ion is bivalent, this result agrees freely well with the value 1135 obtained by Laqueur and Sackur for its equivalent weight.

H. M. D.

Influence of Temperature on the Solubility of Casein in Alkaline Solutions. T. Brailsford Robertson (*J. Biol. Chem.*, 1908, 5, 147—154).—The solubility of casein in alkaline solutions is increased at temperatures over 40°. This fact is not in harmony with the view that heat increases the degree of hydrolytic dissociation of solutions of the caseinates. Osborne showed that heating increases the alkalinity and electrical conductivity of caseinate solutions; it is, therefore, suggested that the influence of heat on proteins consists, among other things, of shifting equilibria of the type:

$$HX{\cdot}OH + HX{\cdot}OH \rightleftharpoons HXX{\cdot}OH + H_2O$$

in the direction of higher complexes, and that heat coagulation is a result of repeated condensations of this type. The solubility of casein in solutions of various concentrations of potassium hydroxide, lithium hydroxide, and calcium hydroxide at various temperatures is given.

W. D. H.

Products of Hydrolysis of Casein. Zdenko H. Skraup (*Monatsh.*, 1908, 29, 791—798. Compare Abderhalden and Funk, Abstr., 1907, i, 1095).—In the products of hydrolysis of casein with hydrochloric acid, three substances occur, which have the composition of leucylvalylimide. The one is fairly strongly lævorotatory, the second is weakly rotatory, and the third is practically inactive. It is not yet certain whether these compounds are pure or mixtures.

The ether-alcoholic extract of the hydrolysed casein, on distillation, left a residue which was esterified and distilled in a vacuum; three fractions were collected up to 115°, and the residue on extraction with alcohol gave a *substance*, $C_{11}H_{20}O_2N_2$, sintering at 283°, m. p. 289°, $[\alpha]_D - 53{\cdot}0°$ (Abderhalden and Funk give $[\alpha]_D - 44{\cdot}27°$).

The mother liquor from this yielded a *substance*, $C_{11}H_{20}O_2N_2$, forming needle-shaped crystals, m. p. 250°, $[\alpha]_D - 17{\cdot}6°$. The alcoholic extract from which the first substance was obtained yielded, with light petroleum, a third *substance*, $C_{12}H_{20}O_2N_2$, forming crystals, m. p. 275°. The mother liquor from this gave leucine, and amines of the composition of butyl- and amyl-amine. After separating the leucine, the solution furnished a basic aurichloride, $C_4H_{12}NCl_3Au$, m. p. 195° (decomp.), the corresponding hydrochloride of which crystallises only in a vacuum, and a platinichloride, $(C_5H_{13}N)_2,H_2PtCl_6$, large, yellow leaves, m. p. 210° (decomp.); the corresponding hydrochloride crystallises more readily than that prepared from the aurichloride, and both give the carbamide reaction. J. C. C.

Formation of Thymine by Heating Intestinal Nucleic Acid. Katsuji Inouye (*Zeitsch. physiol. Chem.*, 1908, **57**, 313).—If nucleic acid (from the intestines) is burnt, a white material collects on the walls of the tube. This was collected and identified as thymine.

W. D. H.

Pyrimidines. X. Action of Diazobenzenesulphonic Acid on Thymine, Uracil, and Cytosine. Treat B. Johnson and Samuel H. Clapp (*J. Biol. Chem.*, 1908, **5**, 163—172).—Thymine, uracil, and cytosine all give, in the presence of alkali, a red solution with diazobenzenesulphonic acid. The colour given by thymine is most intense. Substitution in position 3 in the pyrimidine ring prevents the formation of a red colour, and the absence of this colour reaction in nucleic acids (Burian) indicates that thymine, and probably also cytosine and uracil, are linked in nucleic acids at position 3. Whether the pyrimidines are linked to phosphorus, a carbohydrate complex or otherwise, is not yet settled. W. D. H.

Cleavage Products of Nucleic Acid. Phœbus A. Levene (*Zeitsch. physiol. Chem.*, 1908, **57**, 154—156; Hermann Steudel, *ibid.*, 157—160).—Polemical between the two authors, mainly in reference to priority. W. D. H.

Inosic Acid. Phœbus A. Levene and Walter A. Jacobs (*Ber.*, 1908, **41**, 2703—2707).—When hydrolysed with 5% sulphuric acid and the products isolated by means of their barium salts, inosic acid furnishes a complex phosphoric acid, of which two *barium* salts were analysed. The one, $(C_5H_8O_8P)_2Ba_3$, is amorphous, has $[\alpha]_D^{20} + 4{\cdot}4°$, and reduces Fehling's solution on heating, and the other, $C_5H_7O_9PBa,5H_2O$ or $C_5H_9O_8PBa,5H_2O$, forms bundles of needles and readily reduces Fehling's solution. By hydrolysis of inosic acid with 5% potassium hydroxide, 30% of the original phosphoric acid is eliminated. The conclusion is drawn that in inosic acid the carbohydrate forms a glucophosphoric acid with the phosphoric acid, and that the base is combined with the aldehyde group of the sugar. The authors are unable to confirm the observations of Neuberg and Brahn (Abstr., 1907, i, 1097), or of Bauer (Abstr., 1907, i, 1098), as to the nature of the sugar. J. C. C.

Hydrolysis of Witte's Peptone. Phœbus A. Levene and D. D. van Slyke (*Biochem. Zeitsch.*, 1908, **13**, 440—457).—The peptone was hydrolysed by hydrochloric acid. The following yields of amino-acids were obtained (in parts per cent. of the peptone), the corresponding yields from fibrin being given in brackets: tyrosine, 3·25 (3·3); glycine, 0·78 (2·2); alanine, 2·83 (3·1); valine and leucine, 14·70 (13·0); phenylalanine, 2·60 (1·2); glutamic acid, 8·24 (6·6); aspartic acid, 1·70 (1·7); proline, 4·56 (2·4); serine, 1·18; histidine, 0·75; lysine, 2·71; arginine, 1·48. Total yield of amino-acids, 47·78%. S. B. S.

Polypeptides Containing Tryptophan. Emil Abderhalden and Louis Baumann (*Ber.*, 1908, **41**, 2857—2860).—*Iodoacetyl*-l-*tryptophan*, prepared by coupling the components in alkaline solution, crystallises in needles, m. p. 175—176° (decomp.), and has $[\alpha]_D^{20}+31·3°$. Chloroacetyl-*l*-tryptophan has $[\alpha]_D^{20}+32·9$, not $-32·9°$ as previously stated in error (Abstr., 1907, i, 652). *Methyl*-dl-*α-iodopropionyl*-l-*tryptophan* crystallises in needles aggregated in rosettes, m. p. 145—146°. d,l-*Alanyl*-l-*tryptophan anhydride*, prepared by the action of methyl-alcoholic ammonia on the foregoing, crystallises in minute needles, m. p. 290° (corr.), $[\alpha]_D^{20}+87°$. E. F. A.

Plastein. Phœbus A. Levene and D. D. van Slyke (*Biochem. Zeitsch.*, 1908, **13**, 458—474).—The plastein was made by treatment of a 20% solution of Witte's peptone in 0·2% hydrochloric acid. It was submitted to hydrolysis, and the following percentages of amino-acids were obtained, the corresponding numbers for fibrin being given in brackets: tyrosine, 3·03 (3·1); glycine, 0·50 (2·2); alanine ? (3·1); valine and leucine, 15·59 (13·0); phenylalanine, 1·0 (1·2); glutamic acid, 10·02 (6·8); aspartic acid, 2·15 (1·7); proline, 2·55 (2·4); histidine, 0·43; arginine, 2·06; lysine, 1·42. Total yield of amino-acid, 38·75%. The numbers indicate that plastein is a complex protein, not far removed in composition from fibrin. It is not possible to determine, however, whether the plastein is a synthetic product, or a coagulated form of one of the fibrin albumoses.

S. B. S.

Organic Chemistry.

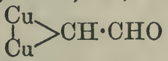
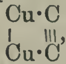
A New Reaction of Petroleum. Ettore Molinari and P. Fenaroli (*Ber.*, 1908, **41**, 3704—3707).—It has been found that Russian petroleums yield ozonides by the action of ozonised oxygen at 8—10°. An oil, b. p. 135—290°, gave 12% of ozonide, whereas one boiling at 295—300° gave 32%. The ozonide forms a white or pale yellowish-red powder soluble in ether, chloroform, or benzene. It can be kept for several days at low temperatures, but decomposes rapidly at 20°, and at 45—50° yields a soft, red substance which is converted into a brown resin at 150°.

The analyses of the ozonide agree with the conclusion that it is derived from a naphthene, $C_{17}H_{20}$, containing two ethylene linkings.

A Roumanian oil gave a similar ozonide, whereas an Italian oil, b. p. 140—265°, gave a small amount of an ozonide, probably derived from a hydrocarbon, $C_{15}H_{16}$.

The ozone also produces a certain amount of oxidation, and the residue left after the removal of the ozonide is still optically active, indicating that this activity cannot be due to unaltered cholesterol in the original oil. J. J. S.

Preparation of Acetylene Di- and Tetra-chlorides. Johann H. Lidholm (D.R.-P. 201705).—A mixture of 2 vols. of chlorine and 1 vol. of acetylene, diluted with 10% of carbon dioxide, reacts quite quietly to furnish acetylene tetrachloride with about 10% of acetylene dichloride when exposed to radium emanations or to the light from a quartz-mercury lamp fed with a current of 3 to 5 amperes and 60—75 volts. G. T. M.

Constitution of Copper Acetylide. Johannes Scheiber [with R. Flebbe] (*Ber.*, 1908, **41**, 3816—3828).—Makowka has assigned the constitution  $\begin{matrix}Cu\\|\\Cu\end{matrix}\!>CH\cdot CHO$ to the copper acetylene compound obtained by precipitation of a cuprous salt by acetylene (this vol., i, 328). It is now shown that the freshly-prepared compound can be converted into a dehydrated form, C_2Cu_2, by heating for two hours at 100° over calcium chloride (compare Keiser, Abstr., 1892, 1416). This result is not in accordance with the aldehyde formula. Further, no acetaldehyde can be detected when the compound is dissolved in hydrochloric acid, whereas trichloromercuriacetaldehyde yields the aldehyde, but no acetylene, under corresponding conditions (Biltz and Mumm, Abstr., 1905, i, 2). It would also appear that the water is firmly held in the molecule, as after drying in a desiccator for twenty-eight days it still has $1H_2O$. Inasmuch as the compound is amorphous, it is unlikely that the compound contains water of crystallisation, and of two suggested formulæ,  $\begin{matrix}Cu\cdot C\\|\quad|||\\Cu\cdot C\end{matrix},H_2O$ and $CH\vdots CCu\cdot CuOH$, preference is given to the latter.

The carbonaceous residue left after dissolution of the acetylide in hydrochloric acid is not an impurity, but is due to secondary changes. Analysis of one preparation led to the formula $(C_{11}H_8O_4)x$, but it is uncertain whether it is of definite composition. W. R.

Hydrogenation of Linalool by means of Nickel and Hydrogen. Synthesis of Tetrahydrolinalool (βζ-Dimethyloctan-ζ-ol). C. J. ENKLAAR (*Rec. trav. chim.*, 1908, **27**, 411—417. Compare this vol., i, 664).—When linalool is directly hydrogenated in the presence of nickel at 130—140°, βζ-dimethyloctane (compare Willstätter and Meyer, this vol., i, 383) is obtained together with the saturated alcohol, tetrahydrolinalool, $C_{10}H_{22}O$, b. p. 88—88·5°/14 mm., D_4^{15} 0·8360, n_D^{15} 1·4388, which is identical with βζ-dimethyloctan-ζ-ol,

$$CHMe_2\cdot[CH_2]_3\cdot CMe(OH)\cdot CH_2Me,$$

prepared synthetically from methylheptenone (Barbier and Bouveault, Abstr., 1896, i, 445; Verley, Abstr., 1898, i, 557; Leser, Abstr., 1898, i, 512; Tiemann, Abstr., 1898, i, 374; Ipatieff, Abstr., 1901, i, 256) by the following series of reactions: methylheptenone reacts with magnesium ethyl iodide to form *βζ-dimethyl-Δ^β-octene-ζ-ol*,

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot CH_3,$$

b. p. 94—94·5°, D_4^{15} 0·8695, n_D^{15} 1·4569, which, on direct hydrogenation in the presence of nickel, yields βζ-dimethyloctan-ζ-ol; it follows therefore that linalool has the formula,

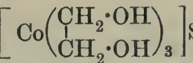
$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH{:}CH_2,$$

ascribed to it by Tiemann and Semmler (Abstr., 1895, i, 646). M. A. W.

α-Methylallyl Alcohol (Δ^α-Butene-γ-ol). ALFRED WOHL and M. S. LOSANITSCH (*Ber.*, 1908, **41**, 3621—3622. Compare Reif, this vol., i, 847).—The action of magnesium methyl iodide on acraldehyde in ethereal solution leads to the formation of α-methylallyl alcohol, $CH_2{:}CH\cdot CHMe\cdot OH$, which is obtained as a viscid, colourless oil, b. p. 96—97°/756 mm. or 28—31°/35 mm., does not reduce ammoniacal silver or Fehling's solution, and when treated with permanganate is only partly oxidised, evolving carbon dioxide. Neither by this reaction nor by oxidation of the unsaturated alcohol with chromic acid and very dilute sulphuric acid can the corresponding ketone be obtained. G. Y.

Complex Compounds of Multivalent Alcohols. A Class of Cyclic Complex Metallic Salts. ADOLF GRÜN and F. BOCKISCH (*Ber.*, 1908, **41**, 3465—3478).—αβ-Glycols and glycerol show a marked tendency to combine with metallic salts. Such compounds are regarded as having a cyclic structure, and are classed with the saccharates formed by sugars with metallic oxides. Ethylene glycol displaces water from the hydrates of copper, cobalt, nickel, and chromium salts, $C_2H_4(OH)_2$ replacing $2H_2O$.

Diethyleneglycolcuprosulphate, $CuSO_4,2C_2H_4(OH)_2,2H_2O$, prepared by warming the constituents together on the water-bath, crystallises in minute, bright blue needles, which melt to a clear blue liquid. On warming at 60°, it loses 25% of its weight, but still contains 11·3% of water. On prolonged heating at 125°, copper sulphate alone remains.

Triethyleneglycolcobaltosulphate,  $\left[\mathrm{Co}\begin{pmatrix}\mathrm{CH_2{\cdot}OH}\\ \mathrm{CH_2{\cdot}OH}\end{pmatrix}_3\right]\mathrm{SO_4,H_2O}$, is best obtained by heating the constituents at the water-bath temperature, diluting the saturated, purplish-red solution with a little alcohol after cooling, and adding acetone until the solution is decolorised. A red oil is precipitated, which forms minute, red, hygroscopic crystals on drying over sulphuric acid. It decomposes in aqueous solution, or on heating to 80°.

Glycerol monomethyl ether (*a-monomethylin*), prepared by the action of sodium methoxide on *a*-monochlorohydrin in cold methyl-alcoholic solution, forms a colourless, pleasant ethereal-smelling liquid, less viscid than glycerol. It has b. p. 196°/728 mm., 115—120°/18 mm.

Dimethylincobaltosulphate, $\mathrm{CoSO_4,2CH_3{\cdot}O{\cdot}CH_2{\cdot}C_2H_3(OH)_2}$, prepared by mixing the components in the cold and precipitating the saturated solution with ether, is obtained as a dark red, microcrystalline mass, which is very hygroscopic.

Glycerol gives rise to compounds with metallic sulphates having the general formula $\left[\mathrm{M}\begin{pmatrix}\mathrm{HO{\cdot}CH_2}\\ \mathrm{HO{\cdot}CH{\cdot}CH_2OH}\end{pmatrix}_3\right]\mathrm{SO_4,H_2O}$.

They are obtained by heating glycerol on the water-bath with the hydrated salt, and precipitated from the saturated solution by means of alcohol.

Triglycerolcuprisulphate is a clear, blue mass of the consistence of colophony. *Triglycerolcobaltosulphate* forms a red, gelatinous mass, which melts on heating; it dissolves in water, and is reprecipitated unchanged by alcohol. *Triglycerolnickelosulphate* is obtained as a transparent, emerald-green, glass-like mass, which is very hygroscopic, but extremely stable. Barium chloride removes the sulphate from this compound, and the corresponding *chloride* results, which is very similar in appearance. *Triglycerolzincisulphate* is an amorphous, colourless mass.

Triglycerol calcium hydroxide forms slightly yellow, granular crystals, which are very hygroscopic and absorb carbon dioxide with great avidity. It dissolves easily in water, sparingly in methyl or ethyl alcohol, all three solutions having an alkaline reaction.

The compounds formed between borates and glycerol in the ordinary analytical procedure are considered to be complex salts of the above type, and not salts of the hypothetical glyceroboric acid.

On mixing boric acid, glycerol and lithium carbonate, and precipitating with alcoholic silver nitrate, bright yellow crystals of the *silver* salt, $\mathrm{AgBO_2,2C_3H_5(OH)_3}$, are obtained.

$\alpha\beta$-Glycols, when treated with hydrogen iodide, are only partly converted into alkyl iodide, the rest being reduced to hydrocarbon. They cannot therefore be estimated in this manner. E. F. A.

Alkylated Halohydrin and Vinylethyl Ethers. JOSEF HOUBEN (*Ber.*, 1908, 41, 3708—3712).—Polemical. A reply to Hoering (this vol., i, 497). J. J. S.

Metallic Salts of Organic Acids. I. Formates and Acetates of Chromium. ALFRED WERNER [with J. JOVANOVITS, G. ASCHKINASY, and J. POSSELT] (*Ber.*, 1908, 41, 3447—3465).—The author has commenced a systematic examination of the capacity of the metallic salts of organic acids to form complex compounds. The present communication deals mainly with the formates and acetates of chromium. Two types of salts have been obtained: (*a*) normal salts; (*b*) complex salts.

The normal salts are prepared by triturating *dihydroxotetra-aquochromium sulphate*, $\left[\mathrm{Cr}{}^{(\mathrm{OH})_2}_{(\mathrm{OH}_2)_4}\right]_2\mathrm{SO}_4$ (which is obtained by the addition of pyridine to an aqueous solution of chromium alum and sodium sulphate), with an organic acid. In this way *hexa-aquochromium formate*, *acetate*, *propionate*, and *butyrate* have been prepared, $[\mathrm{Cr}(\mathrm{H_2O})_6](\mathrm{O\cdot CO\cdot R})_3$. The colour of these salts varies in a remarkable way, the formate being greyish-green, the acetate bluish-violet, the propionate Turkey-blue, and the butyrate silver-grey. The acetate is identical with Recoura's compound (Abstr., 1899, ii, 661), but contains 6 instead of 5 H_2O. All the salts are hydrolytically dissociated by excess of water, giving bluish-green solutions, from which sodium sulphate precipitates dihydroxotetra-aquochromium sulphate. By trituration with mineral acids, the salts are converted into the corresponding hexa-aquochromium salt of the mineral acid, proving that the organic acid group is in the ionogenic state.

The complex salts are of the type $\left[\mathrm{Cr}_3{}^{(\mathrm{OH})_2}_{(\mathrm{O\cdot CO\cdot R})_6}\right]\mathrm{X},x\mathrm{H_2O}$, the constitution of the metallic complex being as yet unknown.

Hexaformatodioltrichromium formate, $\left[\mathrm{Cr}_3{}^{(\mathrm{OH})_2}_{(\mathrm{O\cdot COH})_6}\right]\mathrm{O\cdot COH},5\mathrm{H_2O}$, is prepared by dissolving freshly-precipitated, moist chromium hydroxide in formic acid, D 1·15—1·20 (compare Häussermann, Abstr., 1895, i, 15). By solution in concentrated nitric acid, the air-dried formate is converted into the *nitrate*, $\left[\mathrm{Cr}_3{}^{(\mathrm{OH})_2}_{(\mathrm{O\cdot COH})_6}\right]\mathrm{NO_3},5\mathrm{H_2O}$, from which the corresponding *chloride*, *bromide*, *iodide*, *sulphate*, *dithionate*, and *aurichloride* have been prepared. The free *base*,

$$\left[\mathrm{Cr}_3{}^{(\mathrm{OH})_2}_{(\mathrm{O\cdot COH})_6}\right]\mathrm{OH},5\mathrm{H_2O},$$

obtained from the nitrate and ammonium hydroxide, crystallises in light green needles.

Hexa-acetatodioltrichromium nitrate, $\left[\mathrm{Cr}_3{}^{(\mathrm{OH})_2}_{(\mathrm{O\cdot COMe})_6}\right]\mathrm{NO_3},6\mathrm{H_2O}$, is prepared by dissolving equal quantities of recently-precipitated chromium hydroxide in nitric acid (1 mol.) and in glacial acetic acid (6 mols.) respectively, and heating the mixed solutions on the water-bath until a pure dark green colour is produced; the nitrate slowly separates, after cooling, in tufts of dark green leaflets. The corresponding *chloride*, *bromide*, *iodide*, *periodide*, *aurichloride*, and *platinichloride* are described; the last three salts contain only $5H_2O$. *Hexapropionatodioltrichromium chloride*, $\left[\mathrm{Cr}_3{}^{(\mathrm{OH})_2}_{(\mathrm{O\cdot CO\cdot C_2H_5})_6}\right]\mathrm{Cl},5\mathrm{H_2O}$, forms dark green crystals.

Hexa-acetatodiolamminetrichromium thiocyanate,

$$\left[{}^{\mathrm{NH_3}}_{\mathrm{CNS}}\mathrm{Cr}_3{}^{(\mathrm{OH})_2}_{(\mathrm{O\cdot COMe})_6}\right],$$

prepared from chloropentamminechromium chloride, aqueous potassium thiocyanate, and glacial acetic acid, separates from acetone in tufts of glistening, pale green needles. The thiocyanate group is probably within the metallic complex, since an aqueous solution of the salt does not immediately precipitate silver thiocyanate by treatment with silver nitrate. The mother liquor contains *hexa-acetatodiol-aquo-amminetricobalt nitrate*, $\left[\begin{matrix}NH_3\\H_2O\end{matrix}Cr_3\begin{matrix}(OH)_2\\(O\cdot COMe)_6\end{matrix}\right]NO_3$, which is also obtained by oxidising the thiocyanate with concentrated nitric acid; the corresponding *iodide* is also described. C. S.

Double Compounds of Acetates with Acetic Anhydride. HARTWIG FRANZEN (*Ber.*, 1908, **41**, 3641—3644).—When a recently fused and powdered acetate is boiled for a short time with acetic anhydride and the filtered solution allowed to cool, crystals of a compound of the acetate and anhydride separate. Two series of compounds appear to exist, namely, $(Ac\cdot OR)_2,Ac_2O$ and $Ac\cdot OR,Ac_2O$; the latter have been obtained only in the case of potassium and sodium acetate. The conditions according to which the one or the other compound is produced are unknown in the case of sodium acetate, but in general the compound $(Ac\cdot ONa)_2,Ac_2O$ is formed when crystallisation begins in the warm solution, whilst the compound $Ac\cdot ONa,Ac_2O$ is obtained when crystallisation is started in a super-cooled solution. The acetic anhydride may be combined with the acetate in a manner similar to that of water of crystallisation, or the compounds may be regarded as salts of acetylorthoacetic acids, thus: $NaO\cdot CMe(OAc)_2$ and $CMe(ONa_2)\cdot O\cdot CMe(OAc)_2$. This explanation may throw some light on the constitution of bimolecular fatty acids; thus bimolecular acetic acid may be an acetylorthoacetic acid, $CMe(OH)_2\cdot OAc$.

The *compound*, $(CH_3\cdot CO_2Na)_2,(CH_3\cdot CO)_2O$, forms compact, colourless crystals, m. p. 160°, becoming solid on further heating. It loses acetic anhydride gradually in a vacuum desiccator. The *compound*, $CH_3\cdot CO_2Na,(CH_3\cdot CO)_2O$, forms slender, colourless, matted needles, sintering at 80°, m. p. 150—160°; at 180—200°, the substance boils and begins to solidify, and the whole is completely solid at 220°. It loses acetic anhydride rapidly in a vacuum desiccator.

The *compound*, $(CH_3\cdot CO_2K)_2,(CH_3\cdot CO)_2O$, forms slender, colourless crystals; evidence of the existence of the *compound*,

$$CH_3\cdot CO_2K,(CH_3\cdot CO)_2O,$$

is also adduced. The *compound*, $(CH_3\cdot CO_2Rb)_2,(CH_3\cdot CO)_2O$, forms slender, colourless crystals. The *compound*, $(CH_3\cdot CO_2Cs)_2,(CH_3\cdot CO)_2O$, is also obtained in colourless crystals. J. C. C.

Preparation of the Esters of the Amino-α-hydroxy-acids. LES ETABLISSEMENTS POULENC FRÈRES and ERNEST FOURNEAU (D.R.-P. 198306).—The esters of the amino-α-hydroxy-acids having the general formula $NRR'\cdot CH_2\cdot CMe(OH)\cdot CO_2R''$ (where R'' is an alkyl group and R and R' either hydrogen atoms or alkyl groups) are produced by the esterification of the corresponding acid with aliphatic alcohols in the presence of mineral acids. The starting point in these syntheses is chloroacetone, which, when treated successively with hydrocyanic acid and hydrolytic agents, furnishes β-chloro-α-hydroxy*iso*butyric acid, $OH\cdot CMe(CH_2Cl)\cdot CO_2H$. This chloro-acid, on treatment under pressure with ammonia or primary or secondary aliphatic amines, gives rise to a series of amino-α-hydroxy*iso*butyric acids. The following compounds are described: *Ethyl β-amino-α-hydroxy*iso*butyrate*,

$$OH\cdot CMe(CH_2\cdot NH_2)\cdot CO_2Et,$$

oil, b. p. 107—109°/15 mm.; *hydrochloride*, needles, m. p. 105°; *urethane* derivative, $OH\cdot CMe(CH_2\cdot NH\cdot CO_2Et)\cdot CO_2Et$, b. p. 164—165°/16 mm. *Methyl β-dimethylamino-α-hydroxy*iso*butyrate*,

$$OH\cdot CMe(CH_2\cdot NMe_2)\cdot CO_2Me,$$

oil, b. p. 107°/35 mm.; *hydrochloride* of its *benzoyl* derivative, m. p. 149—150°. *Ethyl β-dimethylamino-α-hydroxy*iso*butyrate*,

$$OH\cdot CMe(CH_2\cdot NMe_2)\cdot CO_2Et,$$

oil, 88—89°/16 mm., 108—110°/32 mm.; the *hydrochlorides* of its *benzoyl* and iso*valeryl* derivatives melt respectively at 137° and 134—135°. iso*Amyl β-dimethylamino-α-hydroxy*iso*butyrate*,

$$OH\cdot CMe(CH_2\cdot NMe_2)\cdot CO_2\cdot C_5H_{11},$$

b. p. 121°/12 mm.; the *hydrochloride* of its *benzoyl* derivative, m. p. 134°. *β-Methylamino-α-hydroxy*iso*butyric acid*,

$$OH\cdot CMe(CH_2\cdot NH\cdot CH_3)\cdot CO_2H,$$

m. p. 230—231°; *ethyl* ester, b. p. 112°/38 mm.

*β-Diethylamino-α-hydroxy*iso*butyric acid*, $OH\cdot CMe(CH_2\cdot NEt_2)\cdot CO_2H$, transparent prisms, m. p. 223°; *ethyl* ester, m. p. 212°/760 mm.

*Propyl β-dimethylamino-α-hydroxy*iso*butyrate*, b. p. 94°/13 mm.; *hydrobromide* of its iso*valeryl* derivative, m. p. 165°. G. T. M.

Oxalyl Chloride. HERMANN STAUDINGER (*Ber.*, 1908, **41**, 3558—3566).—Oxalyl chloride (Fauconnier, Abstr., 1892, 588) is obtained in a 50% yield by the action of phosphorus pentachloride (2 mols.) on anhydrous oxalic acid (1 mol.). It is considered that the intermediate product of the reaction cannot be the half-chloride, as this is unstable at −80°, but may be a compound, $C_2O_2(OPCl_4)_2$, corresponding with that of oxalic acid with antimony pentachloride (Rosenheim and Loewenstamm, Abstr., 1902, i, 358). Oxalyl chloride forms white crystals, m. p. −12°, b. p. 64°/763 mm., reacts quantitatively with water, yielding carbon dioxide, carbon monoxide, and hydrogen chloride, but forms oxalic acid when treated in the gaseous state with water vapour, and is converted into oxalates by alcohols and into oxamides by amines. It is stable towards fuming sulphuric acid, but decomposes, forming carbonyl chloride and carbon monoxide, when distilled through a glass tube heated at 600°, or when boiled with aluminium chloride in carbon disulphide solution, and may therefore be employed in place of carbonyl chloride in the Friedel-Crafts synthesis. When treated with hydrogen sulphide in ethereal solution, oxalyl chloride remains unchanged, but if quinoline is added, carbon monoxide is evolved.

The action of ethyl mercaptan on oxalyl chloride in cold ethereal solution leads to the formation of *ethyl dithio-oxalate*, $C_2O_2(SEt)_2$, which is obtained as a viscid, yellow oil, b. p. 238—240°/757 mm., solidifying at 24—25° to light yellow crystals. G. Y.

Electrolytic Decomposition of Dicarboxylic Organic Acids: Pimelic Acid. B. LINO VANZETTI (*Atti R. Accad. Lincei,* 1908, [v], **17**, ii, 331—333. Compare Abstr., 1907, i, 823).—When neutral salts of the normal acids of the oxalic acid series are electrolysed, lengthening of the carbon atom-chain of the acids is accompanied by increasing complexity of the secondary phenomena of anodic oxidation. Synthesis occurs, owing to the demolition of the anion as it becomes discharged at the anode, alcohols and unsaturated acids being formed, together with their esterification products, hydroxy-acids and lactones, and substances containing aldehydic and ketonic carbonyl groups, formed by the action of the anodic oxygen. Further, with succinic acid, ethylene is formed in appreciable quantity, whilst glutaric acid yields a little propylene, and adipic acid small amounts of two butylenes having normal carbon atom-chains; suberic acid, however, does not yield hydrocarbons in appreciable quantity. Variation of the conditions of electrolysis never leads to the formation of the corresponding cyclic hydrocarbons, tri-, tetra-, and hexa-methylene, which would be expected if the two CO_2 groups of the anion leave the latter simultaneously.

In the case of pimelic acid, now studied, the electrolytic decomposition products consist of ethylene and propylene in approximately equal proportions, and of other compounds analogous with those formed with suberic acid. No *cyclo*pentane is obtained, although the closing of the carbon atom-ring should take place more readily with five carbon atoms than in the other cases. T. H. P.

Diethylmalonic Anhydride. HERMANN STAUDINGER and E. OTT (*Ber.*, 1908, **41**, 3829—3830).—By purifying crude diethylmalonic anhydride by extraction with ether during forty-eight hours, it has decomp. 95—97°, and gives only a very slight depression of the freezing point in benzene solution. It is therefore very highly polymerised, and the conclusion previously drawn that it is higher than duodecimolecular is confirmed (this vol., i, 603). W. R.

Carbon Suboxide. IV. OTTO DIELS and LEONID LALIN (*Ber.*, 1908, **41**, 3426—3434).—Carbon suboxide shows little tendency to combine with aldehydes, hydrogen cyanide, or the Schiff bases; additive compounds with formic acid and with acetic acid have been obtained. In liquid sulphur dioxide at $-40°$ to $-50°$, carbon suboxide and formic acid combine to give a white, crystalline *additive* compound,

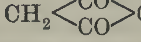
$$C_3O_2,2H{\cdot}CO_2H,$$

which is stable in the absence of moisture, and can be recrystallised from acetyl chloride, formic acid, or methylal and light petroleum. Water instantly decomposes the substance, formic and malonic acids being formed. The molecular formula is established by analysis and by titration with sodium hydroxide (4 equivalents). The constitutional formula is still doubtful; the authors incline to the formula

$$CO_2H{\cdot}C(OH){:}C{:}C(OH){\cdot}CO_2H.$$

The substance melts at 78°, gives off a gas, mainly carbon monoxide, just above the m. p., resolidifies, and again melts at 133—134°, the

m. p. of malonic acid; various other products, however, are also obtained.

The additive compound of carbon suboxide and acetic acid, obtained in a similar manner, has not yet been thoroughly examined. It is a faintly coloured syrup, which, in a vacuum at the ordinary temperature, evolves acetic anhydride, leaving a viscous residue, probably malonic anhydride,  $CH_2<\begin{matrix}CO\\CO\end{matrix}>O$, since it is converted by water into nearly the quantitative amount of malonic acid. C. S.

Preparation of Arylthioglycollic [Arylthiolacetic] Acids. KALLE & Co. (D.R.-P. 199619).—Aromatic compounds containing a reactive halogen or nitro-group interact with alkali thiolacetates to give rise to arylthiolacetic acids, in which the reactive substituent is displaced by the radicle $S{\cdot}CH_2{\cdot}CO_2H$.

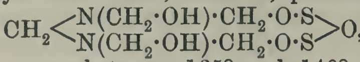
p-*Nitrophenylthiolacetic acid*, $NO_2{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, yellow needles, m. p. 152°, was obtained by heating in alcoholic soda solution, *p*-chloronitrobenzene and thiolacetic acid.

o-*Nitrophenylthiolacetic acid*, m. p. 157°, was similarly prepared from *o*-chloronitrobenzene.

2 : 4-*Dinitrophenylthiolacetic acid*, yellow needles, m. p. 167—168°, was produced from 1-chloro-2 : 4-dinitrobenzene. The crude dinitrobenzene from the mother liquors of crystallised *m*-dinitrobenzene, when condensed in this way with *a*-thiolacetic acid, gave rise to *o*-nitrophenylthiolacetic acid. G. T. M.

New Reaction of Formaldehyde. F. TODTENHAUPT (*Chem. Zeit.*, 1908, **32**, 1045).—When a strong solution of formaldehyde is added to a concentrated ammonium sulphide solution, the mixture becomes heated, and, after a few seconds, there separates a white, soft, sticky substance which, when cooled, forms white, glassy, resinous material with a lustrous fracture; m. p. about 45°. It is soluble in hot glacial acetic acid and in chloroform, and from the former solution, long, white needles separate, m. p. 208°. When heated, the substance (m. p. 45°) has the property of dissolving large quantities of sulphur, becoming brown in colour. J. V. E.

Hyposulphites. V. Rongalitic Acid, Bases, and Formaldehyde. ARTHUR BINZ and ED. ISAAC (*Ber.*, 1908, **41**, 3381—3387. Compare Reinking, Dehnel, and Labhardt, Abstr., 1905, i, 261).—Sodium formaldehydesulphoxylate is termed *Rongalite* by the Badische Anilin- & Soda-Fabrik, and the author uses the name *Rongalitic acid* for the corresponding acid.

When aqueous solutions of ammonium chloride, rongalite, and formaldehyde are mixed, a white, powdery substance, $C_5H_{12}O_5N_2S_2$, probably  $CH_2<\begin{matrix}N(CH_2{\cdot}OH){\cdot}CH_2{\cdot}O{\cdot}S\\N(CH_2{\cdot}OH){\cdot}CH_2{\cdot}O{\cdot}S\end{matrix}>O$, is formed.

It decomposes between 135° and 140°, reduces indigo-carmin, and when kept for some time undergoes spontaneous decomposition, yielding sulphur dioxide. It is also decomposed by hot water. When suspended in boiling alcohol and decomposed by the addition of a small amount of water, it yields aminomethylsulphurous acid, m. p. 193° (compare Reinking, Dehnel, and Labhardt, *loc. cit.*).

Rongalite, aniline hydrochloride, and formaldehyde react in aqueous solution and yield a colourless compound, $C_{25}H_{28}O_4N_4S_2$, m. p. 138—142°, which rapidly decomposes and turns yellow. The compound appears to be formed by the action of rongalite on the hydrochloride of anhydro-*p*-aminobenzyl alcohol, obtained by the action of formaldehyde on aniline hydrochloride. The salts of other primary amines behave in much the same manner as aniline hydrochloride.

Aqueous solutions of rongalite and aniline hydrochloride react in the absence of formaldehyde, and when the mixture is heated in a boiling water-bath it yields a colourless precipitate, $C_{27}H_{32}O_6N_4S_2$, m. p. 159—160°. When thoroughly dried, it remains colourless, but otherwise turns yellow. It does not reduce indigo-carmin, and when heated with acetic anhydride and water yields diacetaminodiphenylmethane.

Dimethylaniline hydrochloride, rongalite, and formaldehyde, when heated together in aqueous solution, yield a *base*, *tetramethyldiaminobenzylphenylsulphone*, $C_{17}H_{22}O_2N_2S$, which crystallises from alcohol or benzene in long needles, m. p. 199°. It does not reduce indigo-carmin, but reacts with nitrous acid, yielding a *nitro-nitroso*-derivative,

$$C_{16}H_{18}O_4N_4S,$$

m. p. 170°. J. J. S.

Action of Bromine on Ether. Bromoacetaldehyde. Charles Mauguin (*Compt. rend.*, 1908, **147**, 747—749).—The action of dry bromine on dry ethyl ether has been investigated by Löwig (*Ann. Phys. Chem.*, 1829, **16**, 376), Völckel (*Annalen* 1842, **41**, 119), and Schützenberger (*Bull. Soc. chim.*, 1873, [ii], **19**, 8). The author has studied the reaction in the presence of water. A mixture of ethyl ether (60 grams), bromine (10 grams), and water (30 grams) is decolorised by one hour's exposure to July sunlight. The velocity of the reaction depends on the intensity of the light (it does not occur in the dark), and is diminished by reducing the quantity of water present. When the reaction is complete, the ethereal layer gives the reactions of an aldehyde, and reacts with urethane, forming bromoacetaldehyde diurethane, m. p. 146°, $CH_2Br\cdot CH(\cdot NH\cdot CO_2Et)_2$, described by Bischoff (*Ber.*, 1872, **5**, 85) and by Hantzsch (Abstr., 1894, i, 363). This urethane gives the aldehyde on distillation with 10% sulphuric acid, and the latter is identified by transformation into glycollaldehyde and glyoxalosazone in the manner described by Fischer and Landsteiner (Abstr., 1892, 1424). The reaction affords a method of readily preparing bromoacetaldehyde. E. H.

The Tricarbon Series. Alfred Wohl (*Ber.*, 1908, **41**, 3599—3612).—Studies in the synthesis of oxygenated acyclic derivatives of propane.

1. *Derivatives of Propaldehyde*.—[With H. Schweitzer.]—*β*-Hydroxypropaldehyde, obtained in small yield by hydrolysis of *β*-hydroxypropaldehydediethylacetal (Abstr., 1900, i, 627) by means of dilute sulphuric acid, has b. p. 75—78°/12 mm. (corr.) (90°/10 mm.:

Nef, Abstr., 1905, i, 3), reduces cold ammoniacal silver nitrate solutions, but not Fehling's solution until after the lapse of some days, when it has commenced to undergo condensation with formation of $\alpha\beta$-unsaturated aldehydes.

β-Iodopropaldehydedimethylacetal, $CH_2I\cdot CH_2\cdot CH(OMe)_2$, prepared by heating the β-chloro-compound with potassium iodide in methyl-alcoholic solution in a sealed tube at 100°, forms a colourless oil, b. p. 85°/60 mm., has an intense odour, and is comparatively stable.

α-Bromopropaldehydedimethylacetal, $CHMeBr\cdot CH(OMe)_2$, prepared by bromination of propaldehydedimethylacetal, is obtained as an oil, b. p. 52°/12 mm. Attempts to prepare α-hydroxypropaldehydeacetal from this or from the diethylacetal were unsuccessful.

2. *Derivatives of αα-Dichloroacetone.*—[With A. Köppen.]—*αα-Dichloroacetonediethylacetal*, $CHCl_2\cdot C(OEt_2)\cdot CH_3$, prepared by Claisen's method (Abstr., 1898, i, 421), is obtained as a liquid, b. p. 76°/8 mm. or 183—184°/767 mm., has an odour resembling camphor, and is miscible with the usual organic solvents.

αα-Dichloroacetonedimethylacetal, $C_5H_{10}O_2Cl_2$, forms a colourless liquid, b. p. 63°/9 mm. or 170—171°/767 mm., and resembles the diethylacetal.

3. *Derivatives of Dichloro*iso*propyl Alcohol.*—[With H. Roth.]—The action of sodium methoxide or ethoxide on dichloro*iso*propyl alcohol leads to the formation of mixtures of derivatives containing varying amounts of chlorine. The *benzoyl* derivative, formed by heating the alcohol with benzoyl chloride, has b. p. 92—94°/0·15—0·17 mm.; this also, when treated with sodium methoxide, yields mixtures of products which cannot be separated.

s-*Tetrachlorodi*iso*propylformal*, $CH_2(O\cdot CHMe\cdot CHCl_2)_2$, prepared by Henry's method (Abstr., 1905, i, 558), has b. p. 81°/0·2 mm., and when treated with sodium methoxide or ethoxide yields a *product*, b. p. 80—300° (indefinite), which reduces Fehling's solution and decolorises permanganate.

4. *Lactaldehyde.*—[With M. Lange.]—*Lactaldehyde*, $C_3H_6O_2$, obtained by hydrolysis of *lactaldehydeacetal* (see following abstract) by means of dilute sulphuric acid, crystallises in flat needles, sinters at 101°, m. p. 105° on prolonged heating, has a bitter flavour, gives a yellow to brown coloration with alkalis, and reduces Fehling's and Tollen's solutions in the cold. When heated under 9 mm. pressure in a bath at 115—125°, the aldehyde distils, chiefly at 58—66°, yielding a mobile distillate which rapidly becomes viscid, undergoing polymerisation. Rosaniline gives a red coloration with the freshly distilled aldehyde in ten seconds, with the crystallised aldehyde in one minute, and with the viscid polymeride, seven days after distillation, in two minutes; the three colorations are of equal depth in ten minutes. In freshly prepared aqueous solution, the aldehyde is bimolecular, and gradually becomes unimolecular, slowly at the ordinary temperature, but more quickly when heated. The *phenylhydrazone*, prepared from the acetal, crystallises in prismatic leaflets, m. p. 90—92°, or when prepared from the aldehyde, m. p. 128—129°; the corresponding *acetol*, m. p. 97—98°. The osazone is identical with methylglyoxalosazone. The *nitrophenylhydrazone* crystallises in yellow prisms, m. p. 124° (corr.); the corresponding *acetol*, m. p. 190—191°. G. Y.

Synthesis of Lactaldehyde. Alfred Wohl and M. Lange (*Ber.*, 1908, 41, 3612—3620).—Ethyl diethoxyacetate is obtained in a 69·5% yield from dichloroacetic acid by a modification of Schreiber's method (*Jahresb.*, 1870, 641), or in a 52% yield by the action of alcoholic hydrogen chloride on calcium glyoxylate. The *piperidide*, $CH(OEt)_2 \cdot CO \cdot C_5NH_{10}$, prepared by boiling the ester with piperidine, forms a viscid, colourless, strongly refracting oil, b. p. 87—90°/0·12—0·15 mm., and when treated with magnesium methyl iodide in ethereal solution yields the aldehydeacetal of methylglyoxal,

$$COMe \cdot CH(OEt)_2,$$

which is obtained as a colourless liquid, b. p. 54—55°/13—15 mm. (corr.) or 161·7—161·8°/761 mm. (corr.), D 0·937. In sodium hydrogen carbonate solution, it forms a *monosemicarbazone*, white needles, m. p. 132°, and in acid solution, a *disemicarbazone*, m. p. 254° (corr.) (compare Harries and Türk, Abstr., 1905, i, 413). With phenylhydrazine in hot acetic acid solution, the acetal yields methylglyoxalosazone. When treated with alkalis, the acetal forms a *polymeride*, b. p. 158—159°/16 mm., and on reduction with sodium and alcohol yields *lactaldehydeacetal*, which is obtained as a clear, mobile liquid, b. p. 67°/12—13 mm. (corr.) or 167—170°/758 mm. (corr.) (slight decomp.). G. Y.

Desmotropy and Merotropy. Arthur Michael (*Annalen*, 1908, **363**, 20—35).—An attempt to refer to the laws of entropy, the phenomena of desmotropy, the existence of two isomerides which can change each into the other by intramolecular wandering of a hydrogen atom, and of merotropy, the formation of derivatives of an isomeride by a substance of stable constitution. It is considered that a correct theoretical view of the whole field can be gained only if the two classes of phenomena are kept strictly separated (compare following abstracts). G. Y.

Tertiary Amines as Reagents for Distinguishing between Stable Enolic and Ketonic Derivatives. Arthur Michael and Howard D. Smith (*Annalen*, 1908, **363**, 36—63).—Hantzsch and Dollfuss drew attention (Abstr., 1902, i, 223, 675) to the advantage of employing trimethylamine instead of ammonia as a reagent for the recognition of ψ-acids, as an addition of the base to a carbonyl group appeared improbable. They found, however, that their expectations as to the solubilities of trimethylammonium salts in ether and benzene were in many cases not fulfilled. In the present work a rise in temperature on addition of the substance to the reagent, and the formation of a new compound, are taken as the signs of chemical reaction. This method is independent of the solubilities of the substances concerned, and permits of the study of the problem without the introduction of complications by the use of a solvent. As triethylphosphine and trimethylamine unite with carbon disulphide, the formation of similar additive compounds of tertiary amines with aldehydes and ketones was not impossible, but is found not to take place.

A number of stable enolic and ketonic compounds have been investigated as to their behaviour towards triethyl-, tripropyl-, trimethyl-, tri*iso*amyl-, tri*iso*butyl-, and tribenzyl-amines. These bases are found to be incapable of enolising stable ketonic compounds. They differ in their capacity to form ammonium salts with enolic compounds, as this property depends on their structure. This capacity is found to diminish in the order in which the bases are named: tri*iso*butylamine reacts only with the most acid enolic compounds, whilst tribenzylamine does not in any case form an ammonium salt. Triethyl- and tripropyl-amines are to be preferred as reagents, because the formation of their additive compounds is accompanied by the development of the greatest amounts of heat, and because they form the most stable salts, an advantage in the case of feebly acid enolic compounds.

The behaviour of merotropic compounds towards amines is discussed, and the conclusion is drawn that a merotropic compound has the enolic form if it reacts with a tertiary amine in absence of a solvent, and the original substance is again formed by the action of hydrochloric acid on the product, but that it has the ketonic form if, whilst not reacting with tertiary amines, it yields with primary and secondary amines, products from which the parent substance is again formed by treatment with hydrochloric acid.

The matter is less simple in the case of desmotropic compounds. The experimental results show that, as was to be expected on theoretical grounds when the conditions of stability of the enolic and the ketonic forms approximate to each other ($K \rightleftarrows E$), the ketonic form is enolised by tertiary amines, and consequently forms ammonium salts. The action of triethylamine on the ketonic form of dibenzoylacetylmethane leads to the formation of an unstable ammonium salt of the enolic form, which undergoes intramolecular transformation into a stable salt, also of the enolic form. It is considered that the tertiary base acts in the first place on the acetyl carbonyl, which possesses the most energy (see Claisen, Abstr., 1896, i, 557), forming the salt, $CBz_2{:}CMe\cdot O\cdot NHEt_3$, the tendency towards better intramolecular neutralisation then causing the triethylammonium group to wander to the benzoyl carbonyl, $CBzAc{:}CPh\cdot O\cdot NHEt_3$. As was to be expected, the enolic form of dibenzoylacetylmethane forms only one salt with triethylamine.

The behaviour of desmotropic compounds of the group $K \rightleftarrows E$ towards tertiary amines agrees with the theoretical expectation, the enolic forms being converted into the ketonic. The ketonic forms of ethyl diacetyl- and dibenzoyl-succinates contain each two asymmetric carbon atoms; Knorr considered (Abstr., 1899, i, 673) therefore that the two forms in which each of these esters are obtained are racemic and inactive modifications. This view is tenable no longer, as Michael and Murphy found (Abstr., 1906, i, 179) that the ketonic modification of dibenzoylacetylmethane, which does not contain an asymmetric carbon atom, also exists in two forms. The ketonic form of ethyl diacetylsuccinate behaves in the same manner as that of dibenzoylacetylmethane towards tertiary amines; the modification melting at the higher temperature is converted, completely by triethylamine, partly by tri*iso*butylamine, into the modification melting at the lower temperature. The enolic modification of ethyl dibenzoylsuccinate, which is only slowly and partly ketonised by sodium carbonate solution (Knorr, *loc. cit.*), is transformed rapidly by traces of triethylamine, forming a mixture of the two ketonic forms. The conditions of stability of the ketones are the converse of those of the acetyl compounds, in that the modification, m. p. 75°, is transformed by triethylamine partly into the modification, m. p. 128°, whereas this is stable towards triethylamine.

The question whether merotropic ketones, which are stable towards tertiary amines alone, can be enolised by these in conjunction with an organic solvent has also been studied. It is found that an organic solvent has no influence on the enolisation of stable merotropic ketones at the ordinary temperature. This conclusion and the classification of many of the substances investigated as ketonic compounds are in disagreement with views which have been founded on the results of physico-chemical investigations. In the present state of their development, however, physical methods cannot be relied on for the decision of such problems, and views founded on the results obtained by these methods can be accepted as correct only when in agreement with the results of chemical investigations.

Ketones.—Diacetylmethane, diacetylethane, acetylheptoylmethane, benzoylacetylmethane, and dibenzoylmethane, oxalyldiacetone, oxalyldimesityl oxide, oxalyldiacetophenone, ethyl acetoacetate, methylacetoacetate, ethylacetoacetate, benzoylacetate, $\alpha\gamma$-diphenyl acetoacetate, benzoylsuccinate, succinylsuccinate, acetonedicarboxylate, acetylmalonanilate, and cyanoacetate are stable towards tertiary amines in the absence of a solvent. In some cases, solution takes place on heating with triethylamine or on treatment with a concentrated solution of the base, but the unchanged ketone is then regained on cooling or on evaporation at the ordinary temperature. Ethyl diacetoacetate, which is stable towards tertiary amines, reacts with primary and secondary amines, forming carbonyl *additive* compounds.

Ethyl oxalacetate is converted by tertiary amines into ethyl oxalocitrolactone (Wislicenus and Beckh, Abstr., 1897, i, 397). *Methyl oxalocitrolactone*, $C_{11}H_{12}O_9$, obtained in the same manner from methyl oxalacetate, forms white crystals, m. p. 63°; the *triethylammonium*, m. p. 103°, *tripropylammonium*, m. p. 88—89°, and *barium*, m. p. 225—227°, salts are described.

Ethyl methyloxalacetate and triethylamine form, with development of heat, a brown *oil*, from which the original ester cannot be regained.

Enolic Compounds.—The following compounds react with tertiary amines with development of heat:

Ethyl α-hydroxymethylenepropionate forms unstable *salts*, which decompose in a vacuum, yielding the ester.

Hydroxymethyleneacetophenone forms oily *products*, which, on treatment with hydrochloric acid, yield a nitrogen-free *substance*, m. p. 73—74°, gradually becoming resinous.

Hydroxymethylenecamphor reacts with triethyl-, tripropyl-, and tri*iso*amyl-amines, but not with tri*iso*butylamine, forming *oils*.

With triethylamine, ethyl phenyloxalacetate forms a colourless, viscid *oil*, $(C_{14}H_{16}O_5)_2,NEt_3$, from which hydrochloric acid liberates the original ester.

Ethyl acetylpyruvate reacts with trimethylamine in benzene-toluene solution, forming a yellow *oil*, which solidifies when rubbed. Similar yellow oils are formed also with other tertiary amines, but only slowly with tri*iso*butylamine. The action of hydrochloric acid on these oily salts leads to the formation of Claisen and Stylos's decomposition product (Abstr., 1887, 918), but of copper acetate in concentrated aqueous-alcoholic solution to the formation of the copper derivative of the pyruvate.

Tetric acid yields a white, crystalline *triethylammonium*,

$$(C_5H_6O_3)_2,NEt_3,$$

m. p. 30—35°, and an oily *tri*iso*amylammonium* salt.

With tertiary bases, ethyl acetylmalonate and benzoylacetoacetate form *salts*, which decompose slowly in a vacuum.

Ethyl dibenzoylacetate does not react with tripropyl-, tri*iso*amyl-, or tri*iso*butyl-amine, but yields a yellow, crystalline *trimethylammonium*, m. p. 75—80°, and a *triethylammonium*, $C_{18}H_{16}O_4,NEt_3$, m. p. 69—70°, salt, decomposing slowly in a vacuum.

In contrast to ethyl diacetylacetate, which is a stable lactone, diacetylacetanilide behaves as an enolic compound, forming an oily *salt* with triethylamine.

Triacetylmethane forms *salts* with trimethyl- and triethyl-amine, but not with other tertiary bases.

The yellow *trimethylammonium* salt of benzoyldiacetylmethane is unstable; the *triethylammonium* salt, $C_{12}H_{12}O_3,NEt_3$, m. p. 55—58°, decomposes slowly in a vacuum.

Ethyl hydroxymethyleneacetoacetate and diacetylhydroxymethylenemethane form moderately stable, red and dark green oily *salts* with triethylamine.

Methyl oxalylsuccinate combines with tertiary fatty amines, with the exception of tri*iso*butylamine, forming *oils*, from which hydrochloric acid liberates apparently the parent ester.

Ethyl acetonedioxylate forms with trimethylamine a yellow salt, m. p. 81—83°, with triethyl-, tripropyl-, and tri*iso*amyl-amines, yellow *oils*, which are decomposed by hydrochloric acid with formation of the parent ester, and with tri*iso*butylamine in benzene, a yellow solution which deposits a red *oil* not decomposed by dilute hydrochloric acid.

The *triethylammonium* salt of ethyl acetophenoneoxalate,

$$C_{12}H_{12}O_4,NEt_3,$$

forms a white, crystalline mass, m. p. 57°. This ester combines with other tertiary amines, forming *oils*.

Methyl dioxalylsuccinate combines with all tertiary amines, including tri*iso*butylamine.

Phloroglucinol yields a *methylammonium*, m. p. 165—167°, *ethylammonium*, $(C_6H_6O_3)_2NEt_3$, m. p. 103—104°, *propylammonium*, m. p. 87—91°, iso*amylammonium*, m. p. 97—100°, and *tri*iso*butylammonium*, m. p. 103—107°, salt. This behaviour, in conjunction with the known reactions of phloroglucinol, is in agreement with the conception of it as a hydroxydiketotetrahydrobenzene.

Phloroglucinol diethyl ether combines with tertiary amines slowly in absence of a solvent, forming colourless *oils*, which are formed more rapidly by treatment of the ether with the tertiary amine in benzene and evaporation of the solution.

Ethyl phloroglucinoldicarboxylate forms a *triethylammonium* salt, $C_{12}H_{14}O_7,NEt_3$, m. p. 101°, which decomposes moderately quickly in a vacuum.

Enol-ketone Desmotropic Compounds.—The enolic modification of methyl mesityloxidoxalate ($K \rightleftarrows E$) combines with triethylamine, forming a yellow, oily *salt*, which gradually decomposes in a vacuum, yielding the enolic ester. The ketonic modification does not react with tertiary amines.

The enolic modification of dibenzoylacetylmethane ($K \rightleftarrows E$) reacts with trimethylamine in toluene solution at – 15°, forming yellow, hexagonal prisms, m. p. 94—97°; this salt, which remains unchanged for some days at 0° in a sealed tube, but decomposes rapidly when exposed to air at the ordinary temperature, is formed also, but more slowly, by the action of the base on the ketonic modification of dibenzoylacetylmethane in toluene solution at – 10°. Both modifications give a transient, yellow coloration, and, thereafter, a colourless, crystalline *product* when treated with the base in ethereal solution at – 15°. The ketonic modification reacts with triethylamine alone or in toluene solution, forming a yellow *salt*, $C_{17}H_{14}O_3,NEt_3$, m. p. 86—90°; in ethereal solution, this is at first formed, but changes into colourless crystals. Tripropylamine also transforms the ketone, forming the *ammonium* salt of the enolic modification. On the other hand, whilst the enolic modification is indifferent to tri*iso*amyl- and tri*iso*butylamines, these bases slowly enolise the ketone.

The enolic modification of tribenzoylmethane ($K \rightleftarrows E$) forms yellow *salts* with trimethyl- and triethyl-amines; whilst the action of tri*iso*amylamine leads partly to the formation of a *salt*, partly to ketonisation of the enol, the latter action alone takes place in presence of tri*iso*butylamine. The ketonic modification is indifferent to tertiary amines alone, or in presence of benzene or ether at the ordinary temperature.

The enolic modifications of ethyl benzylidenebisacetoacetate ($K \rightleftarrows E$) are transformed by tertiary bases into the ketonic form, which is stable towards these reagents. G. Y.

Phenylcarbimide as Reagent for Determining the Constitution of Merotropic Compounds. ARTHUR MICHAEL and PHILIP H. COBB (*Annalen*, 1908, **363**, 64—93).—Dieckmann, Hoppe, and Stein found (Abstr., 1905, i, 135) that the reactivity of phenylcarbimide is greatly increased by the presence of traces of an alkali, and concluded that if such traces are excluded the carbimide does not react with stable ketones, such as the acyclic 1 : 3-dicarbonyl compounds, or with hydroxymethylene derivatives, and that under these conditions phloroglucinol is not attacked, or is attacked only with great difficulty (compare Goldschmidt, Abstr., 1905, i, 340). Michael, on the other hand, found phloroglucinol to react readily with phenylcarbimide in cold ethereal solution (Abstr., 1905, i, 195). The present authors have therefore again studied the action of phenylcarbimide on ketones, carrying out the experiments partly in glass tubes boiled out with water and acids, and partly in platinum apparatus, and taking all precautions as to the purity of the substances employed. It is found that at the ordinary temperature ethyl acetoacetate and ethyl phenylhydroxymethyleneacetate form *C*- and *O*-additive compounds respectively, whilst at 100° phloroglucinol readily forms the compound obtained by Dieckmann, Hoppe, and Stein only in presence of alkalis. An observation that a specimen of phenylcarbimide containing phenylcarbylamine is less reactive than the pure reagent may explain the differences in the results obtained by the different investigators.

Only certain ketones are capable of reacting with phenylcarbimide; dibenzoylmethane, for example, is indifferent to this reagent. The chemical potential necessary for the reaction $CH_2R\cdot COR' + NPh\dot{:}CO = NHPh\cdot CO\cdot CHR\cdot COR'$ must depend on the nature of the substituting groups R and R′. The formation of the additive compound takes place directly, and not by way of an intermediate *O*-derivative, as is shown by the formation of an *additive* compound by ethyl β-diethylaminocrotonate,

$$NEt_2\cdot CMe\dot{:}CH\cdot CO_2Et \longrightarrow NEt_2\cdot CMe\dot{:}C(CO_2Et)\cdot CO\cdot NHPh.$$

On treatment with concentrated sulphuric acid, the additive compound yields diethylamine and the additive compound of phenylcarbimide and ethyl acetoacetate; hence addition can take place directly to an unsaturated methenyl group.

It has been found further that, whilst ethyl benzoylacetate reacts with phenylcarbimide, forming ethyl benzoylmalonanilate, ethyl methyl- and ethyl-acetoacetates are indifferent to the reagent even in presence of alkalis.

Whilst ethyl cyanoacetate does not react with phenylcarbimide, the sodiocyanoacetate readily forms an *additive* compound, which, on treatment with hydrochloric acid, yields ethyl cyanomalonanilate, $C_{12}H_{12}O_3N_2$. This crystallises in prisms, m. p. 145°, and is hydrolysed slowly by boiling alkalis, forming cyanoacetanilide.

α-Formylpropionanilide (Abstr., 1905, i, 195) separates from light petroleum in crystals, m. p. 95—96°.

A study of the rise in temperature caused by mixing fatty alcohols with phenylcarbimide gave the following results. The rise in temperature is quoted in degrees; the figures in brackets are the weights in grams of the alcohol and the phenylcarbimide brought into reaction.

Methyl alcohol (0·1 : 0·26), 37°; ethyl alcohol (0·14 : 0·29), 23°; *n*-propyl alcohol (0·1 : 0·3), 23°; (0·17 : 0·32), 28°; *iso*propyl alcohol (0·1 : 0·3), 12°; (0·17 : 0·32), 13°; *n*-butyl alcohol (0·185 : 0·3), 26·5°; (1·0 : 1·6), 47°; *iso*butyl alcohol (0·185 : 0·3), 22°; (1·0 : 1·6), 31°; *tert.*-butyl alcohol (0·185 : 0·3), 5°; (1·0 : 1·6), 4°. The *additive* compounds of the three butyl alcohols crystallise from light petroleum in needles, m. p. 63—64°, 86°, and 134—135° respectively.

The action of phenylcarbimide on ethyl lactate leads to the formation of considerable amounts of carbanilide.

Methyl salicylate does not react with phenylcarbimide at 160°. At 170° the mixture yields only carbanilide, and at 175°, triphenyl*iso*cyanurate. On the other hand, an *additive* compound, $C_{15}H_{13}O_4N$,

m. p. 117°, which is probably identical with Lambling's derivative (Abstr., 1902, i, 756), is formed in two to four days by the action of phenylcarbimide on methyl salicylate at the ordinary temperature in presence of traces of sodium acetate, propylamine, or tributylamine. In some experiments, there was obtained a product, m. p. 238—240° (Snape, Trans., 1885, **47**, 770; 1886, **49**, 254; Smolka and Friedreich, Abstr., 1890, 618). Ethyl salicylate reacts in the same manner as the methyl ester. The *additive* compound, $C_{16}H_5O_4N$, formed in two hours in presence of traces of sodium acetate, separates from carbon disulphide in crystals, m. p. 98—100°.

In presence of sodium acetate, the *iso*butyl ester and phenylcarbimide form triphenyl *iso*cyanurate.

In contrast to the salicylates, methyl *m*- and *p*-hydroxybenzoates react with phenylcarbimide in the absence of a catalyst at the ordinary temperature. The *additive* compound of the *m*-ester, $C_{16}H_{15}O_4N$, separates from benzene in crystals, m. p. 115—116°; the *additive* compound of the *p*-ester, m. p. 134—135°.

The authors have studied also the behaviour of phenylcarbimide towards phenols and anilines containing negative substituting groups or atoms (compare Gumpert, Abstr., 1885, 656; 1886, 342). It is found that the reaction is hindered more by a nitro-group in the ortho- than by a nitro-group in the para-position. *o*-Nitrophenol reacts with phenylcarbimide only at 150—170°, traces of an additive compound being formed. At the ordinary temperature, the carbimide slowly polymerises, and the urethane is not formed. *p*-Nitrophenol and phenylcarbimide, on the other hand, react slowly at the ordinary temperature, forming the *urethane*, $C_{13}H_{10}O_4N_2$, which crystallises in yellow prisms; polymerism of the reagent does not take place.

Picric acid does not react with phenylcarbimide.

Both *o*- and *p*-chlorophenols react more readily than does *p*-nitrophenol; o-*chlorophenyl phenylcarbamate*, $C_{13}H_{10}O_2NCl$, separates from benzene in crystals, m. p. 120—121°.

Quantitative experiments with the three nitroanilines show that the meta-compound reacts most easily, the ortho-compound least so. Similarly, the velocity of the formation of o-*chlorodiphenylcarbamide*, needles, m. p. 181—182°, from *o*-chloroaniline and phenylcarbimide can be followed by titration, but not that of the meta- or the para-compound, which takes place with too great rapidity.

The dihydroxybenzenes do not react with phenylcarbimide in ethereal solution at the ordinary temperature; the mixture gradually forms small amounts of the polymeride of the carbimide. G. Y.

Acetyl Chloride and Acetic Anhydride as Reagents for Distinguishing between Enolic and Ketonic Modifications.

ARTHUR MICHAEL and ARTHUR MURPHY, jun. (*Annalen*, 1908, **363**, 94—106).—The formation of an acetate by the action of acetyl chloride on a carbinol, R·OH, takes place in two stages, the first being the formation of an additive compound, R·O·CMeCl·OH, and the second, the splitting off of hydrogen chloride. The ease with which the first stage, and therefore the whole reaction, takes place depends on the nature of the group R, and the reaction may be entirely prevented if R is sufficiently negative. It is for this reason that the stable enolic compounds, ethyl acetylmalonate and benzoylacetoacetate, are not acetylated by acetyl chloride or acetic anhydride, whilst benzoyldiacetylmethane remains unattacked by acetyl chloride even in pyridine solution. Similarly, the enolic forms of desmotropic compounds of the groups $K \rightleftarrows E$ and $K \underset{\swarrow}{\rightarrow} E$ are not acetylated by acetyl chloride, but are dissolved and ketonised by the reagent. On the other hand, a ketonic modification may be acetylated by acetyl chloride if the ketone carbonyl possesses sufficient chemical potential for the chloride to form the additive compound, $OAc \cdot CRCl \cdot C_nH_{2n+1}$, and if the conditions are favourable to the splitting off of hydrogen chloride from this, when the acetyl derivative of the enolic modification must be formed; hence acetylation of a merotropic compound by acetyl chloride or acetic anhydride cannot be looked on as evidence of the existence of the substance in the enolic form.

When acetic anhydride is employed, there is the further disadvantage that reaction takes place usually only at high temperatures (150—200°), when intramolecular transformation is still more probable, especially as it is difficult under such conditions to exclude sodium acetate, which Dieckmann, Hoppe, and Stein have shown (Abstr., 1905, i, 135) to act catalytically even in traces. This disadvantage is avoided by employing acetyl chloride at temperatures below 100°, but, although under these conditions enol-acetyl derivatives are not obtained from the ketonic modifications of di- and triacylmethanes, its behaviour with certain other enolic and ketonic compounds shows that acetyl chloride cannot be considered as a trustworthy reagent for determining the constitution of a merotropic compound.

Enolic Compounds.—When heated with acetyl chloride in a reflux apparatus, ethyl acetylmalonate, benzoylacetoacetate, dibenzoylacetate and *C*-acetylmalonanilate, *C*-diacetylacetanilide, benzoyldiacetylmethane, and triphenylvinol remain unchanged. Under the same conditions, ethyl α-hydroxymethylenepropionate and hydroxymethylenephenylacetate, and hydroxymethylenecamphor form acetyl derivatives. Benzoyldiacetylmethane and triphenylvinol are not acetylated by boiling acetic anhydride.

Ketonic Compounds.—Diacetylmethane, αα-diacetylethane, acetylheptoylmethane, ethyl acetoacetate and diacetoacetate, methyl oxalacetate, *C*-dibenzoylacetanilide, ethyl diphenylacetoacetate, benzoylacetylmethane, dibenzoylmethane, ethyl benzoylacetate, ethyl methanetricarbmonoanilate, and ethyl benzoylsuccinate remain unchanged, or if attacked do not form acetyl derivatives when heated with acetyl chloride at 100°.

Enol-keto-desmotropism.—The enolic modification of methyl mesityloxidoxalate ($K \rightleftarrows E$) is transformed by acetyl chloride at the ordinary temperature into the ketonic modification, which is obtained together with an oil, insoluble in sodium carbonate, when the enol is heated with acetyl chloride, traces of hydrogen chloride being evolved. Under the same conditions, the ketonic modification remains unchanged.

The ketonic modification of dibenzoylacetylmethane ($K \rightleftarrows E$), m. p. 148°, is formed by the action of acetyl chloride in ethereal solution on the enolic modification, or on the ketonic modification, m. p. 107—110°.

The enolic modification of ethyl diacetylsuccinate ($K \mathrel{\substack{\searrow \\ \swarrow}} E$) is transformed by acetyl chloride into a mixture of the β- and γ-ketonic forms; under the same conditions, the γ-ketone is transformed into the β-ketone, and hence prolonged action of acetyl chloride on the enolic modification leads to the formation of the β-ketone alone.

The ketonic modifications of tribenzoylmethane ($K \mathrel{\substack{\searrow \\ \swarrow}} E$), *p*-bromotribenzoylmethane, and ethyl dibenzoylsuccinate are formed when the enolic modifications are heated with acetyl chloride. Under the same conditions, the ketonic modifications of the two methane derivatives remain unchanged, whilst the γ-ketonic form of the ester, m. p. 75°, is converted into the β-ketonic form, m. p. 128—130°.

G. Y.

Sugars. JAN. J. BLANKSMA AND W. ALBERDA VAN EKENSTEIN (*Chem. Weekblad*, 1908, **5**, 777—781).—*l*-Gulose, *l*-idose, *d*-talose, and *l*-ribose have been isolated by combination with substituted phenylhydrazines, followed by decomposition of the hydrazones by benzaldehyde or formaldehyde. The sugars were obtained in the form of syrups which did not crystallise.

l-Gulose was prepared by reduction of *l*-gulonolactone with sodium amalgam (compare Fischer and Stahel, Abstr., 1891, 667), the sodium hydroxide formed being neutralised periodically with sulphuric acid. After the reduction, the solution was concentrated, the sodium sulphate filtered off, and washed with alcohol to remove the syrup. Evaporation of the alcohol left a syrup containing somewhat less than half the weight of the lactone used. This substance separated out in part after a time, and the rest was removed by dissolving in water, neutralising with barium carbonate, filtering off the barium gulonate, and concentrating the filtrate. On treating the residual syrup with phenylhydrazine, *l*-gulosephenylhydrazone separated in yellow crystals, m. p. 136°. The product recrystallised from water has m. p. 143°. It was boiled in aqueous solution with the calculated quantity of benzaldehyde, the benzaldehydephenylhydrazone filtered off, and the slight excess of benzaldehyde removed by steam. On evaporation, the *l*-gulose remained as a light yellow syrup of sweet taste. It could not be obtained crystalline from either water, methyl alcohol, ethyl alcohol, mixtures of alcohol and water, or of alcohol and ether. When cooled with liquid air, it solidified to a hard, glass-like solid, $[\alpha]_D - 20{\cdot}4°$. Its power of reducing Fehling's solution is 71·5% of that of invert-sugar. These numbers are probably too low, as the syrup contained water. Fischer (*loc. cit.*) states that *l*-gulose is slightly dextrorotatory; that obtained by the authors' method is lævorotatory.

The *methylguloside* was obtained from the syrup by the action of a concentrated solution of hydrochloric acid in absolute methyl alcohol, removal of the hydrochloric acid by lead carbonate, and evaporation of the filtrate. It is a syrup, and has not been crystallised.

Benzylguloside was prepared by a similar method from benzyl alcohol. After long standing, it crystallises, and on recrystallisation from methyl alcohol has m. p. 145°. The quantity was too small to admit of analysis.

l-Idose was obtained by a method analogous to that employed for *l*-gulose, starting from *l*-idonolactone. It is a clear syrup, with $[\alpha]_D$ +7·5°, and a reducing power 43% of that of invert-sugar. It does not combine with substituted phenylhydrazine or benzoylhydrazine.

d-Talose was prepared from talonic acid, obtained by Fischer's method (Abstr., 1892, 299), which yields a mixture of unchanged galactonic acid and talonic acid. The two acids were converted into the corresponding phenylhydrazides, and these separated by repeated crystallisation from alcohol, talonylphenylhydrazide being the most soluble, and separating from the mother liquor in star-shaped or nodular, acicular masses. Talonic acid was obtained from its phenylhydrazide by boiling with baryta water, removing the phenylhydrazine with ether, and adding sulphuric acid (compare Fischer and Passmore, Abstr., 1890, 152). The acid was converted into its lactone by heating on the water-bath, and reduced to *d*-talose with sodium amalgam. The phenylmethylhydrazone was then prepared, and, after repeated crystallisation from methyl alcohol, had m. p. 154°. When boiled in aqueous solution with benzaldehyde, the hydrazone is converted into talose, which forms a colourless syrup, $[\alpha]_D$ +13·95°; reducing power is 71·4% of that of invert-sugar.

l-Ribose was prepared similarly from ribonolactone, but could not be purified by conversion into its phenylhydrazone (compare Fischer and Piloty, Abstr., 1892, 439) or phenylmethylhydrazone, as these compounds are freely soluble in all solvents. The syrup has $[\alpha]_D$ +14°, and a reducing power 55·5% of that of invert-sugar. A. J. W.

Presence of *i*-Dimethylinosite in the Latex of Melabœai from Sumatra. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1908, 27, 257—259).—The liquid expressed from the coagulated latex of *Melaboeai* contains *i*-dimethylinosite, which can be isolated in the form of rectangular crystals, m. p. 206° (Girard, *Compt. rend.*, 1870, 67, 820, gives 195°); the tetra-acetyl derivative has m. p. 195° (Girard, *loc. cit.*, gives 193°). On treatment with hydriodic acid, it yields *i*-inosite, m. p. 222° (Maquenne, Abstr., 1887, 356, gives 217°), which forms a hexa-acetyl derivative, m. p. 217° (Maquenne, Abstr., 1887, 908, gives 212°). M. A. W.

Forms of Lactose. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1908, 30, 1767—1783).—In an earlier paper (Abstr., 1904, i, 974), it has been stated that lactose hydrate crystallises from aqueous solutions of the sugar at the ordinary temperature, whilst at temperatures above 95° the *β*-anhydrous form separates. The present investigation was undertaken with the object of determining the transition temperature between these forms of lactose, and as it was found that the work illustrated very fully the general conditions underlying transition temperatures, the measurements were extended to several related phenomena.

All the results agreed quantitatively with the conclusions obtained previously, namely, that aqueous solutions of lactose contain two substances in equilibrium, and that the mutarotation of lactose results from the gradual establishment of equilibrium of the balanced equation $C_{12}H_{22}O_{11},H_2O \rightleftarrows H_2O + C_{12}H_{22}O_{11}$ (β-modification). It is shown that the hypotheses of hydration and stereoisomerisation which have been advanced to explain the mutarotation of sugars are summed up and reconciled by the following equation, in which the equilibrium of the first balanced reaction is established instantaneously, whilst that of the second is attained gradually, giving rise to the slow change of rotation: α-form $+ H_2O \rightleftarrows$ hydrated form $\rightleftarrows H_2O +$ β-form.

Determinations of the initial and final solubilities of lactose hydrate and β-anhydride between 0° and 100° show that the transition temperature between them is 93°, and this value is confirmed by vapour-pressure measurements. The specific rotatory power of the three forms of lactose has been determined at 15° and 25°, and the results show that the equilibrium in solution does not change perceptibly with the temperature in this interval. It has also been found that the equilibrium does not change with the concentration, since there is no slow change in the rotation of the solutions after dilution. Schmœger has found the rotatory power of the stable solution of lactose at 20° to be 55·3° per gram $C_{12}H_{22}O_{11}$. Accepting this value, the initial specific rotation of the hydrate is 86·0°, and that of the β-anhydride, 35·4°. The freezing points of lactose solutions, the vapour pressures of saturated solutions of lactose hydrate, and the aqueous vapour pressure of the solid hydrate in contact with the β-anhydride are also recorded. The heat of solution of the β-anhydride has been calculated from the solubility data, and found to agree with the value obtained by direct measurement (this vol., ii, 665). The heat of vaporisation of water from the hydrate has been calculated from the vapour pressures of the hydrate, and also from the heats of solution and transition of the two forms, and the two values agree satisfactorily. E. G.

Colloidal Properties of Starch and the Unity of its Constitution. Eugène Fouard (*Compt. rend.*, 1908, **147**, 813—816. Compare this vol., i, 503).—The author has shown previously that a pseudo-solution of starch, when filtered through collodion, is divided into two portions, one consisting of a true solution, the other containing colloidal starch. The experiments described in the present paper confirm the conclusion that starch is a single chemical compound capable of undergoing complete and reversible physical transformation into the state of perfect solution. Thus, when the pseudo-solution is fractionally filtered through a collodion membrane, the successive fractions are found to have the same rotatory power. The residual fractions of the colloid show less tendency to coagulate than the earlier fractions, but this is found to be due to the fact that the traces of mineral phosphates, on the presence of which this phenomenon depends, are not evenly divided between the true solution and the colloidal residue, the last fraction of which is almost neutral to methyl-orange or phenolphthalein.

The conclusion is drawn that the mode of aggregation of the elementary starch molecule is variable, and depends on the reaction of the surrounding plasma, which varies under different conditions. Thus, owing to different influences, such as the age of the cell-wall modifying the osmotic permeability of the membrane, different molecular aggregates of variable resistance are produced, and this gives rise to the concentric layers observed in the natural starch grain. W. O. W.

Action of Ammonium Persulphate Solution on Cellulose. II. The Relation of the Cellulose Peroxide formed to the other Products of the Reaction and the Mechanism of the Process of Oxidation. Reaction of Oxycellulose with Nessler's Reagent. Hugo Ditz (*J. pr. Chem.*, 1908, [ii], **78**, 343—364. Compare Abstr., 1907, i, 829).—As it has been stated that hydrogen peroxide is formed by the decomposition of ammonium persulphate, the action of hydrogen peroxide on cellulose was compared with that of the persulphate. Whilst the action of the latter is accompanied by evolution of much gas, only very little gas is evolved by the action of hydrogen peroxide, and cellulose peroxide is not formed. It is shown that the cellulose peroxide formed by the persulphate method does not contain sulphuric acid. When boiled with water, the peroxide yields a small amount of a flocculent substance, which may be oxycellulose; the acid (acid-cellulose ?) present in the peroxide is insoluble in water. Cellulose peroxide does not evolve ammonia when boiled with lime water, but gives with Nessler's reagent a brown coloration, becoming grey in consequence of the reduction of the mercuric salt by the small amount of oxycellulose present in the peroxide. Oxycellulose contains probably an aldehyde group, as it behaves towards Nessler's reagent in the same manner as a very dilute solution of formaldehyde; it is suggested that the reducing properties of cellulose and hydrocellulose are dependent on the presence of small amounts of oxycellulose (compare Rosenthaler, Abstr., 1906, ii, 911).

The gases evolved by the action of ammonium or potassium persulphate on cellulose are now found to contain carbon dioxide as well as "active" oxygen; the latter is evolved from ammonium persulphate, also, by the action of zinc, tin, or antimony in presence of dilute sulphuric acid; copper, on the other hand, dissolves in ammonium persulphate in presence of dilute sulphuric acid without evolution of "active" oxygen or sulphur dioxide. When 100 c.c. of a 10% solution of ammonium persulphate are heated with filter paper and 5 c.c. of dilute sulphuric acid, and the gases evolved passed into a potassium iodide-starch solution, this becomes violet after eight minutes, and after fifteen minutes requires 0·3 c.c. of $N/10$ sodium thiosulphate solution for decolorisation. A slightly greater effect is produced by employing linen in place of filter paper. Under the same conditions, but in absence of cellulose, the potassium iodide-starch solution is only slightly coloured in eleven minutes, and after twenty-five minutes is decolorised by 0·05 c.c. of $N/10$ sodium thiosulphate. In absence of both cellulose and sulphuric acid, the gases evolved on heating ammonium persulphate solution do not colour potassium iodide-starch solution in twenty-five minutes.

In conclusion, the mechanism of the oxidation of cellulose is discussed, and the formation of oxycellulose is compared with that of formaldehyde when methyl alcohol is heated with a persulphate. The formation of the peroxide may take place by addition of oxygen either directly to the cellulose molecule or secondarily to oxycellulose. G. Y.

Preparation of Sulphonic Esters of Cellulose. Actien-gesellschaft für Anilin Fabrikation (D.R.-P. 200334).—Alkali-soluble cellulose, produced from bleached cotton by the action of zinc chloride and hydrochloric acid, is treated with toluene-*p*-sulphonyl chloride in the presence of 10% aqueous sodium hydroxide. The *toluene*-p-*sulphonic* ester of cellulose separates after twenty hours as a white, amorphous powder, insoluble in acid zinc chloride solution or in cuprammonium solution; it dissolves in hot glacial acetic acid, and its solution in epichlorohydrin, chloroform, or ethyl acetate on evaporation leaves a transparent pellicle. G. T. M.

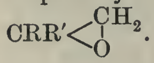
Preparation of Alcohol from Substances containing Cellulose. Theo Koerner (*Zeitsch. angew. Chem.*, 1908, 21, 2353–2359).—The author has endeavoured to ascertain whether the sugar obtained by hydrolysis from wood, etc., by dilute sulphuric acid was entirely derived from the cellulose, or in part from the lignous substances. Comparable experiments with sawdust, straw, and sulphite-cellulose show the amount of alcohol obtained to be proportional to the cellulose present.

It has been stated that sulphurous acid increases the yield of alcohol, but the author finds that such previous treatment actually decreases the amount of alcohol obtainable. As hydrocellulose is found to yield as much as 17·95% of alcohol, it was thought possible that by treating wood, sulphite-cellulose, or straw with oxidising agents before hydrolysis, a similarly increased yield of alcohol might be obtained. With dilute solutions of hydrogen peroxide, this has been realised, the yield of alcohol being materially increased, although in the case of chromic acid a marked decrease is observed. Similarly, the yield of alcohol is found to be decreased by a preliminary oxidation with a solution of potassium persulphate or ozone, the oxidation proceeding beyond the hydrocellulose stage. J. V. E.

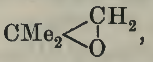
Investigations on the Charring of Wood. II. Peter Klason, Gust. von Heidenstam, and Evert Norlin (*Arkiv. Kem. Min. Geol.*, 1908, 3, No. 10, 1—17. Compare this vol., i, 717).—The charring of wood out of contact with air at a maximum temperature of 400° proceeds mainly according to the equation $2C_{42}H_{60}O_{28} = 3C_{16}H_{10}O_2$ (wood-charcoal) $+ 28H_2O + 5CO_2 + 3CO + C_{28}H_{32}O_9$. The velocity of this change depends on the temperature. Charring begins at about 270°, and increases greatly in rapidity at about 300°. This dry distillation of wood is an exothermic change, the heat of the reaction being about 6% of the heat of combustion; in the case of cellulose, the heat of the reaction is about 5% of that of combustion. The methyl alcohol obtained is formed entirely from the methoxy-groups of the lignin, and the amount obtained from birch or beech wood is about

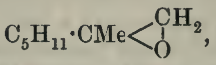
double that yielded by fir or pine. Acetic acid is formed from the cellulose, and also, to a greater extent, from the lignin; birch or beech gives about double as much of the acid as fir or pine. The calorific value of the combustible gases formed during dry distillation is about 3·8% of that of the wood itself; these gases contain neither hydrogen nor aromatic hydrocarbons. Wood charcoal, having the composition $C_{16}H_{10}O_2$, may be regarded as the product of the exothermic charring of wood.
T. H. P.

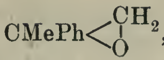
Modification of the Preparation of Methylamine from Bromoacetamide. MAURICE FRANÇOIS (*Compt. rend.*, 1908, **147**, 680—682. Compare this vol., i, 768).—By a modification of the method of preparing methylamine from bromoacetamide described previously, the author is able to obtain a yield of 72% of the theoretical, instead of 35%. The solution of bromoacetamide is prepared by the interaction of acetamide and bromine in presence of water and calcium carbonate, thus avoiding possible loss of bromine through formation of hypobromites or bromates, as when potassium hydroxide is used. The resulting red solution is mixed with cold 30% aqueous sodium hydroxide, and placed in a narrow tube bent several times up and down, which is heated by boiling water. The products are distilled in a current of steam, ammonia is separated by yellow mercuric oxide, and the methylamine distilled off and converted into the hydrochloride.
J. C. C.

Preparation of Amino-alcohols. J. D. RIEDEL (D.R.-P. 199148).—The amino-alcohols, $OH\cdot CRR'\cdot CH_2\cdot NR''R'''$, are obtained by the action of primary or secondary aliphatic amines on the alkylene oxides,  $CRR'<\begin{matrix}CH_2\\|\\O\end{matrix}$.

β-Methylbutylene αβ-oxide, $CMeEt<\begin{matrix}CH_2\\|\\O\end{matrix}$, b. p. 80°/760 mm., prepared from β-methylbutylene chlorohydrin and sodium hydroxide, gives rise to *dimethylaminodimethylethylcarbinol*, $NMe_2\cdot CH_2\cdot CMeEt\cdot OH$, b. p. 57°/23 mm., when treated with dimethylamine in benzene solution at 125°. The *hydrochloride* of the *benzoyl* derivative of this base, m. p. 175°, may be employed as a local anæsthetic.

iso*Butylene αβ-oxide*,  $CMe_2<\begin{matrix}CH_2\\|\\O\end{matrix}$, b. p. 53°/760 mm., prepared from *iso*butylene chlorohydrin, furnishes with dimethylamine the base *dimethylaminotrimethylcarbinol*, $NMe_2\cdot CH_2\cdot CMe_2\cdot OH$, b. p. 160°/48 mm.; the hydrochloride of the benzoyl derivative, m. p. 202°, crystallises from absolute alcohol.

αδ-Dimethylamylene αβ-oxide,  $C_5H_{11}\cdot CMe<\begin{matrix}CH_2\\|\\O\end{matrix}$, b. p. 147°/760 mm., D 0·8416, obtained from αδ-dimethylamylene chlorohydrin by the action of aqueous sodium hydroxide, yields *dimethylaminodimethyliso-amylcarbinol*, $C_5H_{11}\cdot CMe(OH)\cdot CH_2\cdot NMe_2$, b. p. 98—99°/24 mm., on treatment with dimethylamine in benzene solution; the *hydrochloride* of the *benzoyl* derivative of this base separates in silky needles, m. p. 138°.

β-Phenylpropylene αβ-oxide,  $\mathrm{CMePh}<\overset{\mathrm{CH_2}}{\underset{\mathrm{O}}{|}}$, b. p. 93°/33 mm., D 1·0436, obtained from phenylpropylene chlorohydrin, gives rise to *dimethylaminophenyldimethylcarbinol*, b. p. 135—136°/32 mm., *hydrochloride*, needles, m. p. 159—160°, *aurichloride*, m. p. 110°, *benzoyl* derivative, oily, furnishing a *hydrochloride*, prisms, m. p. 205—206°.

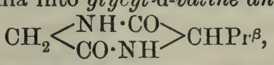
Methylaminophenyldimethylcarbinol, $\mathrm{OH{\cdot}CMePh{\cdot}CH_2{\cdot}NHMe}$, b. p. 135—138°/31 mm., hydrochloride, leaflets, m. p. 153°, *benzoyl* and *dibenzoyl* derivatives both melting at 122°, was obtained from β-phenylpropylene αβ-oxide and methylamine.

Methylaminodimethylethylcarbinol, $\mathrm{OH{\cdot}CMeEt{\cdot}CH_2{\cdot}NHMe}$, b. p. 80°/52 mm., *divaleryl* derivative, oil, b. p. 162°/26 mm., results from the interaction of β-methylbutylene αβ-oxide and methylamine.

G. T. M.

Synthesis of Polypeptides. XXVII. 3. Derivatives of Active Valine. EMIL FISCHER and HELMUTH SCHEIBLER (*Annalen*, 1908, **363**, 136—167).—Only inactive dipeptides of valine have been prepared previously. A knowledge of the optically active forms appeared desirable, not only to permit of a comparison of the synthetical substances with the products of protein hydrolysis, but also for the study of Walden's transformation. Glycyl-*d*-valine, *d*-alanyl-*d*-valine, and *l*-leucyl-*d*-valine are readily prepared in the usual manner by coupling *d*-valine with the chlorides of the halogeno-fatty acids, and treating the products with aqueous ammonia, as are also *d*-α-bromo*iso*valeryl-glycine and *l*-α-bromo*iso*valeryl-*d*-valine by coupling *d*- and *l*-α-bromo*iso*valeryl chlorides with glycine and *d*-valine respectively. In order to avoid racemisation, these bromo-compounds must be converted into the dipeptides by means of anhydrous, liquid ammonia. On hydrolysis, *d*-valylglycine yields *d*-valine and glycine, whilst *l*-valyl-*d*-valine yields *dl*-valine. When treated with ammonia in methyl-alcoholic solution at 0°, the methyl ester of *l*-valyl-*d*-valine yields an inactive anhydride, termed *trans-valine anhydride*.

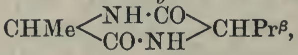
Chloroacetyl-d-*valine*, $\mathrm{CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CHPr^{\beta}{\cdot}CO_2H}$, crystallises from water in prisms, m. p. 113—115° (corr.), or from alcohol in plates; $[\alpha]_D^{20}$ + 15·8°. Glycyl-*d*-valine, $\mathrm{NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CHPr^{\beta}{\cdot}CO_2H}$, separates from aqueous alcohol in microscopic needles, m. p. about 254° (corr.), $[\alpha]_D^{20}$ − 19·7° in aqueous, − 10·5° in hydrochloric acid, and − 6·9° in sodium hydroxide, solution. The *hydrochloride* crystallises in needles or prisms; the *copper* salt separates from its deep blue aqueous solution partly in microscopic prisms and partly as a vitreous mass. The *hydrochloride* of the methyl ester, $\mathrm{C_8H_{16}O_3N_2,HCl}$, prepared by treatment of glycyl-*d*-valine with hydrogen chloride in methyl-alcoholic solution and evaporation of the product at 25° under diminished pressure, crystallises in needles. This is converted by methyl-alcoholic ammonia into *glycyl*-d-*valine anhydride*,



$$\mathrm{CH_2}<\begin{matrix}\mathrm{NH{\cdot}CO}\\\mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CHPr^{\beta}},$$

which crystallises in needles, m. p. about 266° (corr.), $[\alpha]_D^{20}$ + 20·8° in glacial acetic acid, $+32\cdot7^\circ$ in aqueous, or $+41^\circ$ in alcoholic, solution (Fischer, Abstr., 1907, i, 901).

d-*a-Bromopropionyl*-d-*valine*, $\mathrm{CHMeBr\cdot CO\cdot NH\cdot CHPr^{\beta}\cdot CO_2H}$, prepared from *d-a*-bromopropionyl chloride and *d*-valine, forms feathery crystals, m. p. 180° (corr.), $[a]_D^{20}$ $+20\cdot8^\circ$ to $+21^\circ$ in alcoholic solution. d-*Alanyl*-d-*valine*, $\mathrm{NH_2\cdot CHMe\cdot CO\cdot NH\cdot CHPr^{\beta}\cdot CO_2H}$, crystallises from dilute alcohol in microscopic needles, m. p. about 265° (corr.), $[a]_D^{20}$ $-1\cdot9^\circ$ in hydrochloric acid, $-4\cdot5^\circ$ in *N*-sodium hydroxide, or $-5\cdot4^\circ$ in aqueous, solution. d-*Alanyl*-d-*valine anhydride*,

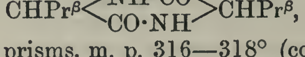


$$\mathrm{CHMe}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CHPr^{\beta}},$$

is prepared by conversion of the dipeptide into its *methyl ester hydrochloride*, and treatment of this with ammonia in methyl-alcoholic solution; it crystallises in needles, m. p. about 268—270° (corr.), $[a]_D^{20}$ $-29\cdot3^\circ$ in glacial acetic acid solution, and has less inclination than the preceding anhydride to separate from its solutions in the gelatinous state.

d-*a-Bromo*iso*hexoyl*-d-*valine*, $\mathrm{CH_2Pr^{\beta}\cdot CHBr\cdot CO\cdot NH\cdot CHPr^{\beta}\cdot CO_2H}$, prepared from *d-a*-bromo*iso*hexoyl chloride and *d*-valine, forms stout crystals, m. p. 150—151°, $[a]_D^{20}$ $+24\cdot3^\circ$ in alcoholic solution. l-*Leucyl*-d-*valine*, $\mathrm{NH_2\cdot CH(C_4H_9)\cdot CO\cdot NH\cdot CHPr^{\beta}\cdot CO_2H}$, crystallises from aqueous alcohol in spears or prisms containing water of crystallisation, which is lost in a vacuum over sulphuric acid, m. p. about 282° (corr.; slight decomp.) when quickly heated, $[a]_D^{20}$ $+18\cdot0^\circ$ in aqueous solution. The *anhydride*, $\mathrm{C_{11}H_{20}O_2N_2}$, formed by way of the *methyl* ester, crystallises in microscopic needles, m. p. about 282°, $[a]_D^{20}$ $-46\cdot5^\circ$ to $-50\cdot2^\circ$ in glacial acetic acid solution.

l-*a-Bromo*iso*valeryl*-d-*valine*, $\mathrm{CHPr^{\beta}Br\cdot CO\cdot NH\cdot CHPr^{\beta}\cdot CO_2H}$, prepared from *l-a*-bromo*iso*valeryl chloride and *d*-valine, crystallises in needles, m. p. 163—165° (corr.), $[a_D^{20}]$ $-22\cdot7^\circ$ in absolute alcohol. l-*Valyl*-d-*valine*, $\mathrm{C_{10}H_{20}O_3N_2,1\frac{1}{2}H_2O}$, crystallises in needles, and loses the water of crystallisation at 95°/12—15 mm. over phosphoric oxide, m. p. about 308° (corr.), $[a]_D^{20}$ $-70\cdot6^\circ$ to $-74\cdot0^\circ$. The *hydrochloride* forms quadratic crystals, and is readily soluble in water. The *hydrochloride* of the methyl ester, formed in the usual manner, crystallises in needles, and on treatment with ammonia in methyl-alcoholic solution is converted into trans-*valine anhydride*,



$$\mathrm{CHPr^{\beta}}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CHPr^{\beta}},$$

which crystallises in prisms, m. p. 316—318° (corr.), and is optically inactive.

d-*Valylglycine*, $\mathrm{NH_2\cdot CHPr^{\beta}\cdot CO\cdot NH\cdot CH_2\cdot CO_2H}$, prepared from *d-a*-bromo*iso*valerylglycine (Fischer and Scheibler, this vol., i, 858) by the action of liquid ammonia at 25°, crystallises from aqueous alcoholic-ethereal solution in short prisms, m. p. about 272° (corr.), $[a]_D^{20}$ $+89\cdot8^\circ$ to $+93\cdot6^\circ$ in aqueous solution, or $[a]_D^{20}$ $+39\cdot4^\circ$ in 10% hydrochloric acid. A by-product of the formation of this dipeptide crystallises on evaporation of the alcoholic-ethereal mother liquor in prisms, and has an acid reaction and taste. G. Y.

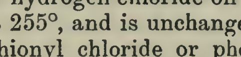
Distillation of Creatinine. R. ENGELAND (*Zeitsch. physiol. Chem.*, 1908, **57**, 65—66).—The following compounds have been isolated from the products obtained by the destructive distillation of creatinine hydrochloride: ammonia, dimethylamine, and pyrrole. J. J. S.

Glycocholic Acid. Maurice Piettre (*Compt. rend.*, 1908, **147**, 810—813).—A convenient method is described for isolating glycocholic acid from pig's bile. The product amounts to 60—75% of the total weight of glycocholic acid present, and is quite free from taurocholic acid; its composition agrees with the formula $C_{27}H_{45}O_6N$. The pure acid has m. p. 150°, and $[\alpha]_D$ $+21°54'$ in alcoholic solution.

Alkali hydroxides have no action on glycocholic acid under ordinary conditions, but under pressure, complicated changes, exceeding the limits of simple hydrolysis, occur. The toxic properties of sodium glycocholate have been determined; with the higher animals, the lethal dose varies according to the method of administration. W. O. W.

Iminodiacetic Acid and some Derivatives. W. J. A. Jongkees (*Rec. trav. chim.*, 1908, **27**, 287—326).—The derivatives of iminodiacetic acid, $NH(CH_2 \cdot CO_2H)_2$ (diglycollamidic acid, iminoacetic acid), described in the original can be divided into three groups: (I) derivatives containing the imino-group; (II) derivatives in which the hydrogen of the imino-group is replaced by acyl radicles, (III) hydantoin derivatives.

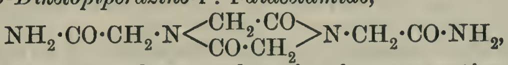
(I). The *hydrochloride* of iminodiacetic acid, $HCl,NH(CH_2 \cdot CO_2H)_2$, obtained by the action of hydrogen chloride on the acid in the presence of alcohol, decomposes at 255°, and is unchanged by the action of such dehydrating agents as thionyl chloride or phosphorus pentachloride; the *ethyl* ester, $HCl,NH(CH_2 \cdot CO_2Et)_2,H_2O$, has m. p. 74°, and, on treatment with alcoholic ammonia, yields *ethyl hydrogen iminodiacetate*, $NH(CH_2 \cdot CO_2H) \cdot CH_2 \cdot CO_2Et$, m. p. 175—176°; the *hydrochloride*, $HCl,NH(CH_2 \cdot CO_2H) \cdot CH_2 \cdot CO_2Et$, has m. p. 143°; the *methyl* ester, $HCl,NH(CH_2 \cdot CO_2Me)_2$, has m. p. 183°, and yields *methyl iminodiacetate*, $NH(CH_2 \cdot CO_2Me)_2$, b. p. 126°/33 mm. or 123·5°/16 mm., $D^{16·5}_{16·5}$ 1·1675, from which the diamide, $NH(CH_2 \cdot CO \cdot NH_2)_2$, m. p. 143° (Heintz, *Annalen*, 1868, **148**, 178), and the *monamide* (*iminoacetamic acid*), $NH(CH_2 \cdot CO_2H \cdot CH_2 \cdot CO \cdot NH_2$, m. p. 210°, are obtained by the action of ammonia; the *hydrochlorides* have m. p. 255° and 210° respectively; and the *compound*, $NH_3,HCl,NH(CH_2 \cdot CO \cdot NH_2)_2$, obtained by treating the hydrochloride of methyl iminodiacetate with methyl-alcoholic ammonia, forms beautiful crystals, that soften at 145°, but do not melt at 190°. *Iminodiacetimide* [2 : 6-*diketopiperazine*],



$$NH{<}{\begin{smallmatrix}CH_2 \cdot CO\\ CH_2 \cdot CO\end{smallmatrix}}{>}NH,$$

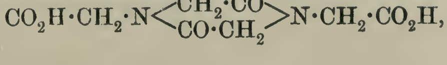
obtained by heating under 15 mm. pressure the ammonium salt, the monamide, or the diamide of the acid, forms white needles, m. p. 200—205°.

(II). 2 : 5-*Diketopiperazine*-1 : 4-*diacetamide*,



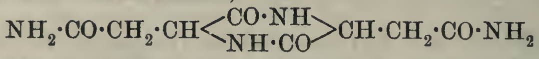
$$NH_2 \cdot CO \cdot CH_2 \cdot N{<}{\begin{smallmatrix}CH_2 \cdot CO\\ CO \cdot CH_2\end{smallmatrix}}{>}N \cdot CH_2 \cdot CO \cdot NH_2,$$

is obtained as a secondary product in the preparation of iminodiacetimide; it decomposes at 303—305°; the *acid*,



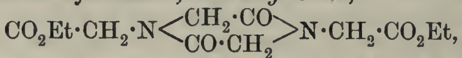
$$CO_2H \cdot CH_2 \cdot N{<}{\begin{smallmatrix}CH_2 \cdot CO\\ CO \cdot CH_2\end{smallmatrix}}{>}N \cdot CH_2 \cdot CO_2H,$$

forms crystals, m. p. 280—290°, and, unlike the isomeride, 2 : 5-diketopiperazine-3 : 6-diacetamide,



$$\mathrm{NH_2\cdot CO\cdot CH_2\cdot CH<\begin{matrix}CO\cdot NH\\NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CO\cdot NH_2}$$

(Fischer, Abstr., 1905, i, 32), is stable towards boiling methyl-alcoholic potassium hydroxide; the *ethyl* ester,



$$\mathrm{CO_2Et\cdot CH_2\cdot N<\begin{matrix}CH_2\cdot CO\\CO\cdot CH_2\end{matrix}>N\cdot CH_2\cdot CO_2Et,}$$

has m. p. 79—80°. *Acetyliminodiacetonitrile*, $\mathrm{NAc(CH_2\cdot CN)_2}$, obtained by the action of acetic anhydride on iminodiacetonitrile, is a viscid oil, b. p. 227°/16 mm.; *methyl acetyliminodiacetate*, $\mathrm{NAc(CH_2\cdot CO_2Me)_2}$, similarly prepared, has b. p. 184—185°/15 mm., m. p. 83·5—84°; *acetyliminodiacetamide*, $\mathrm{NAc(CH_2\cdot CO\cdot NH_2)_2}$, has m. p. 203°, and yields the *hydrochloride*, $\mathrm{HCl,NAc(CH_2\cdot CO\cdot NH_2)_2}$.

Carbmethoxyiminodiacetonitrile, $\mathrm{CO_2Me\cdot N(CH_2\cdot CN)_2}$, prepared from methyl chloroformate and iminodiacetonitrile, has m. p. 63—64°, b. p. 189°/15 mm.; *methyl carbmethoxyiminodiacetate*, $\mathrm{CO_2Me\cdot N(CH_2\cdot CO_2Me)_2}$, has b. p. 167°/15 mm.; *carbmethoxyiminodiacetamide*,

$$\mathrm{CO_2Me\cdot N(CH_2\cdot CO\cdot NH_2)_2,}$$

has m. p. 212°; *carbmethoxyiminodiacetic acid*, $\mathrm{CO_2Me\cdot N(CH_2\cdot CO_2H)_2}$, has m. p. 123°, and the blue *copper* salt, $\mathrm{C_6H_7O_6NCu,H_2O}$, and the *barium* salt, $\mathrm{C_6H_7O_6NBa,H_2O}$, have been prepared.

Methyl chloroformyliminodiacetate, $\mathrm{COCl\cdot N(CH_2\cdot CO_2Me)_2}$, obtained by the action of carbonyl chloride (1 mol.) on methyl iminodiacetate (2 mols.), has m. p. 74°; *methyl carbonyldi-iminodiacetate*,

$$\mathrm{CO[N(CH_2\cdot CO_2Me)_2]_2,}$$

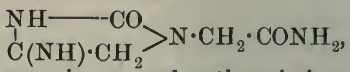
from carbonyl chloride (1 mol.) and methyl iminodiacetate (4 mols.), forms needles, m. p. 88—89°; the *amide*,

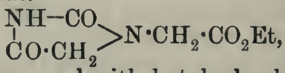
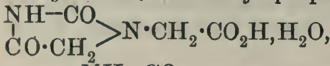
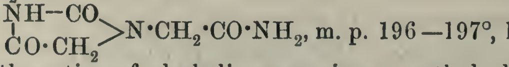
$$\mathrm{CO[N(CH_2\cdot CO\cdot NH_2)_2]_2,}$$

darkens at 230° and decomposes at 250°, and the *nitrile*,

$$\mathrm{CO[N(CH_2\cdot CN)_2]_2,}$$

forms white crystals, m. p. 155°.

(III). 4-*Iminohydantoin*-1-*acetamide*,  $\mathrm{\begin{matrix}NH\text{——}CO\\C(NH)\cdot CH_2\end{matrix}>N\cdot CH_2\cdot CONH_2}$, obtained by the action of alcoholic ammonia on carbmethoxyiminodiacetonitrile, forms colourless needles, which decompose at 245°, and yields a crystalline *hydrochloride*.

Ethyl hydantoin-1-*acetate*,  $\mathrm{\begin{matrix}NH\text{—}CO\\CO\cdot CH_2\end{matrix}>N\cdot CH_2\cdot CO_2Et}$, obtained by hydrolysis of the preceding compound with hot hydrochloric acid and subsequent esterification, forms beautiful needles, m. p. 84—85°; the *methyl* ester, similarly prepared, has m. p. 107—108°; the *acid*,  $\mathrm{\begin{matrix}NH\text{—}CO\\CO\cdot CH_2\end{matrix}>N\cdot CH_2\cdot CO_2H,H_2O}$, forms clear, hydrated crystals; the *amide*,  $\mathrm{\begin{matrix}NH\text{—}CO\\CO\cdot CH_2\end{matrix}>N\cdot CH_2\cdot CO\cdot NH_2}$, m. p. 196—197°, has been prepared (1) by the action of alcoholic ammonia on methyl chloroformyliminodiacetate; (2) as a secondary product in the hydrolysis of iminohydantoin-1-acetamide, and (3) by the action of ammonia on the ethyl ester.

M. A. W.

Hexathiocyano-salts of Molybdenum. Johanna Maas and Julius Sand (*Ber.*, 1908, **41**, 3367—3376. Compare this vol., i, 397, 513).—A reply to the criticism of Rosenheim and Garfunkel (this vol., i, 614). The authors have carefully re-analysed the potassium, ammonium, and zinc ammino-salts, and confirm their previous results.

The *chromihexathiocyanoammonium acetate*,

$$Cr(SCN)_6(NH_4)_3,H_2O,HOAc,$$

prepared from the chloride, $CrCl_2(H_2O)_4Cl,2H_2O$, ammonium thiocyanate, and acetic acid, crystallises in reddish-violet, rhombic needles, isomorphous with the corresponding molybdenum salt. W. R.

Preparation of Additive Compounds of Chloral with Amides. Nathan Sulzberger (D.R.-P. 198715).—Chloral combines additively with the amides of the higher fatty acids. *Chloral palmitinamide*, $CCl_3\cdot CH(OH)\cdot NH\cdot CO\cdot[CH_2]_{14}\cdot CH_3$, an oleaginous, white, crystalline powder, m. p. 110°, is produced by mixing its generators and warming at 100°. *Chloral α-bromopalmitin anilide*, prepared in a similar manner, is a colourless, crystalline powder with a greasy feel.

G. T. M.

Action of Phosphorus Pentachloride on Halogenated Acid Amides. Wilhelm Steinkopf (*Ber.*, 1908, **41**, 3571—3595).—Although in regard to their rates of formation and stability the halogen-substituted acetonitriles and acetamides closely resemble nitroacetamide and -acetonitrile, it is found that they do not yield the corresponding acetimide chlorides when treated with thionyl chloride, whereas, as shown by Steinkopf and Bohrmann (this vol., i, 327), the action of thionyl chloride on nitroacetamides leads to the formation of nitroacetimide chlorides. The author has studied therefore the action of phosphorus pentachloride on dichloro- and dibromoacetonitriles.

Wallach found (this Journ., 1877, ii, 182) that, whilst the action of phosphorus pentachloride on acetamide leads to the formation of the amide chloride, which readily loses hydrogen chloride, forming the imide chloride, di- and tri-chloroacetamides yield products which may have the formulæ (1) $CHCl_2\cdot CO\cdot NCl\cdot PCl_2$ and $CCl_3\cdot CO\cdot NCl\cdot PCl_2$ or (2) $CHCl_2\cdot CCl\colon N\cdot POCl_2$ and $CCl_3\cdot CCl\colon N\cdot POCl_2$ respectively. It is found now that the formation of such phosphorus compounds is a general reaction of the α-halogenated acetamides. The formulæ (2) are to be preferred, as the action of moisture on these compounds leads to the displacement of a chlorine atom by a hydroxyl group, and the formation of a product, $CHCl_2\cdot C(OH)\colon N\cdot POCl_2$, or its tautomeric form, $CHCl_2\cdot CO\cdot NH\cdot POCl_2$, is more probable than that of a product, $CHCl_2\cdot CO\cdot N(OH)\cdot PCl_2$.

[With Czeslau Benedek.]—The liquid product, obtained by the action of phosphorus pentachloride on chloroacetamide in absence of moisture (Wallach, *loc. cit.*), gives, on analysis, figures agreeing with the formula $CH_2Cl\cdot CCl\colon N\cdot POCl_2$; it decomposes on distillation in a vacuum, and, on exposure to moisture, evolves hydrogen chloride and yields small amounts of crystalline chloroacetylphosphamic chloride, $CH_2Cl\cdot CO\cdot NH\cdot POCl_2$.

Dichloroacetylphosphamic chloride, $CHCl_2\cdot CO\cdot NH\cdot POCl_2$, formed by the action of moist air on αββ-trichloroethylidenephosphamic chloride (Wallach, *loc. cit.*), crystallises in white plates, m. p. 112—113°. When treated with sodium ethoxide in alcoholic solution, it forms the *ethyl* ester, $CHCl_2\cdot CO\cdot NH\cdot PO(OEt)_2$, which crystallises in white needles, m. p. 72—73°, is soluble in dilute sodium hydroxide or ammonia, forms a yellow *precipitate* with platinum tetrachloride in ammoniacal solution, and can be titrated with *N*/10 potassium hydroxide. The *dianilide*, $CHCl_2\cdot CO\cdot NH\cdot PO(NHPh)_2$, prepared by heating the oxydichloride with aniline in ethereal solution, or by the successive action of an excess of aniline and of water on αββ-trichloroethylidenephosphamic chloride, crystallises from alcohol in white needles, m. p. 219—220°. The *bisphenylhydrazide*, $CHCl_2\cdot CO\cdot NH\cdot PO(NH\cdot NHPh)_2$, forms white crystals, m. p. 190° (decomp.).

Trichloroacetylphosphamic chloride, $CCl_3\cdot CO\cdot NH\cdot POCl_2$, prepared by evaporating the light petroleum solution of the imide chloride-phosphorus oxydichloride (Wallach, *loc. cit.*) in contact with moist air, crystallises in white needles, m. p. 146—148°, and when treated with water yields phosphoric acid and trichloroacetamide. The *methyl* ester, $CCl_3\cdot CO\cdot NH\cdot PO(OMe)_2$, crystallises in white leaflets, m. p. 105—107°, and dissolves in dilute alkalis; the *potassium* salt, $C_4H_6O_4NCl_3PK$, m. p. about 135°, is hygroscopic. The *ethyl* ester, $C_6H_{11}O_4NCl_3P$, forms crystalline aggregates, m. p. 47—48°. The *dianilide*, $C_{14}H_{13}O_2N_3Cl_3P$, white needles, m. p. 194—195°. The *bisphenylhydrazide*, $C_{14}H_{15}O_2N_5Cl_3P$, m. p. 237—238° (decomp.).

The product of the action of phosphorus pentachloride on bromoacetamide is unstable and has not been isolated.

[With H. Grünupp.]—*Tribromochloroethylidenephosphamic chloride*, $CBr_3\cdot CCl:N\cdot POCl_2$, formed from phosphorus pentachloride and tribromoacetamide at 90—110°, is obtained as a liquid, which gradually crystallises. *Tribromoacetylphosphamic chloride*, $CBr_3\cdot CO\cdot NH\cdot POCl_2$, formed by exposing the preceding substance to air, separates from benzene in crystals, m. p. 105—106°, and decomposes on further exposure to moisture. When treated with sodium methoxide in methyl-alcoholic solution, it forms *methyl dibromomethoxyacetylphosphamate*,

$$OMe\cdot CBr_2\cdot CO\cdot NH\cdot PO(OMe)_2,$$

which separates from water in white crystals, m. p. 92—93°. The corresponding *ethoxy-ethyl* ester, $C_8H_{16}O_5NBr_2P$, forms long needles, m. p. 91°.

[With G. Kirchhoff.]—*αβ-Dichloro-β-bromoethylidenephosphamic chloride*, $CHClBr\cdot CCl:N\cdot POCl_2$, prepared from chlorobromoacetyl compound, is obtained as a yellow liquid. The *amide*, formed by the action of moisture on this, could not be purified, and was converted directly into the *ethyl* ester, $CHClBr\cdot CO\cdot NH\cdot PO(OEt)_2$, colourless crystals, m. p. 67—68°.

αββ-Trichloro-β-bromoethylidenephosphamic chloride,

$$CCl_2Br\cdot CCl:N\cdot POCl_2,$$

prepared from dichlorobromoacetamide, forms crystals, m. p. 68°. The *chloride*, $CCl_2Br\cdot CO\cdot NH\cdot POCl_2$, forms colourless crystals, m. p. 147°;

the *methyl* ester of this, $C_4H_7O_4NCl_2BrP$, separates from water in crystals, m. p. 107°; the *ethyl* ester, m. p. 76—77°.

Dichloronitroacetamide, $NO_2\cdot CCl_2\cdot CO\cdot NH_2$, prepared by the action of chlorine on ammonio-nitroacetamide, is obtained as a white, crystalline precipitate, m. p. 94—95°. The *αββ-trichloro-β-nitrophosphamic chloride*, $NO_2\cdot CCl_2\cdot CCl\colon N\cdot POCl_2$, forms white crystals, m. p. 55—60°. *Dichloronitroacetylphosphamic chloride*, $C_2HO_4N_2Cl_4P$, separates from benzene in crystals, m. p. 165° (decomp.); the *ethyl* ester, $C_6H_{11}O_6N_2Cl_2P$, long needles, m. p. 56°.

α-Chloro-ββ-dibromo-β-nitroacetylphosphamic chloride,

$$NO_2\cdot CBr_2\cdot CCl\colon N\cdot POCl_2,$$

forms white crystals, m. p. about 65°. *Dibromonitroacetylphosphamic chloride*, $C_2HO_4N_2Cl_2Br_2P$, white crystals, m. p. 187—188° (decomp.).

[With C. Benedek.]—*α-Chloro-β-bromophenylethylidenephosphamic chloride*, $CHBrPh\cdot CCl\colon N\cdot POCl_2$, was analysed. The derivatives are unstable.

α-Chlorodiphenylacetamide has m. p. 111—113° (115°: Bickel, Abstr., 1889, 999). *Chlorodiphenylacetylphosphamic chloride*,

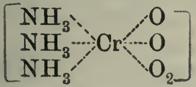
$$CClPh_2\cdot CO\cdot NH\cdot POCl_2,$$

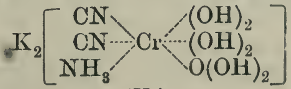
forms crystals resembling ammonium chloride, m. p. 122—123°. The *methyl* ester, $C_{16}H_{17}O_4NClP$, white crystals, m. p. 104—106°.

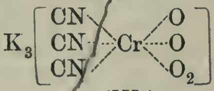
αββ-Trichloropropylidenephosphamic chloride, $CMeCl_2\cdot CCl\colon N\cdot POCl_2$, prepared from di-α-chloropropionamide and phosphorus pentachloride at 85—95°, crystallises from light petroleum in white needles, m. p. 80°. *Di-α-chloropropionylphosphamic chloride*, $C_3H_4O_2NCl_5P$, snow-white needles, m. p. 127—128°.

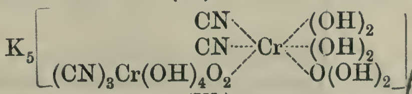
Other nitro-amides, such as nitroacetamide and nitromalonamide, also react with phosphorus pentachloride, but the products are too unstable to permit of their isolation. G. Y.

Higher Oxidation Products of Chromium. IV. Chromium Tetroxide Compounds. Ernst H. Riesenfeld [and, in part, Alfred Wesch] (*Ber.*, 1908, **41**, 3536—3552. Compare Abstr., 1906, ii, 92; this vol., ii, 951; Riesenfeld and Wohlers, Abstr., 1907, ii, 357).—The mol. wt. of Wiede's triamminechromium tetroxide (Abstr., 1898, ii, 28) has been determined by the cryoscopic method, and the values obtained found to agree with the formula $(NH_3)_3CrO_4$ (compare Werner, Abstr., 1906, ii, 760). The structural formula I has been


(I.)


(II.)


(III.)


(IV.)

assigned to this compound; in support of this formula, it has been found possible to prepare the dicyanomonammine derivative, II, intermediate between the tricyano-compound, III, of Wiede (*loc. cit.*) and the triamminechromium tetroxide. A compound has also been prepared having the formula IV, in which one of the positions in the complex is occupied by a group similar in composition to the rest of the complex radicle. This is probably the first complex salt of this nature to be prepared.

The complex in II and IV is represented as containing water, since compound II crystallises with water, which is removed together with ammonia when the substance is kept over calcium chloride, and compound IV crystallises with water, only part of which is eliminated over phosphoric oxide. One mol. of the triammine, when decomposed by acid or alkali, yields 2—3 equivalents of hydrogen peroxide, that is, only the O_2 group in the complex forms hydrogen peroxide, and is thus in all probability a bivalent group. It is therefore highly probable that the chromium in the tetroxide derivatives is sexavalent.

Potassium dichromium tetroxide pentacyanide,

$$K_5[(CrO_4)_2(CN)_5],5H_2O,$$

is formed by treating an aqueous solution of potassium cyanide and chromic acid, cooled in an ice-salt freezing mixture, with hydrogen peroxide; it crystallises in dark reddish-brown prisms. Molecular-weight determinations by the cryoscopic method and electrical conductivity measurements show that the salt when completely dissociated in aqueous solution is ionised, thus: $K_5[(CrO_4)_2(CN)_5] = 5K^{\cdot} + [(CrO_4)_2CN]' + 4CN'$. It is converted by aqueous ammonia into *potassium dicyanomonamminechromium tetroxide*,

$$K_2[CrO_4(CN)_2NH_3],5H_2O,$$

crystallising in long, slender, yellowish-brown needles. The complex of this salt is dissociated in dilute aqueous solution. It slowly evolves hydrogen cyanide and ammonia when kept, and decomposes with slight explosion when heated rapidly. W. H. G.

Preparation of the Cyanides and Cyanamides of the Alkali and Alkaline Earth Metals. BADISCHE ANILIN- & SODA FABRIK (D.R.-P. 200986).—All nitrogen compounds of titanium, such as the nitride or the carbonitrides, readily give rise to cyanides or cyanamides when heated with carbon and the oxides, carbonates, sulphates, or other salts of the alkali and alkaline earth metals. The reaction occurs either in the presence or absence of a fusible medium, such as fusion mixture or a fusible chloride. The carbon may be introduced in the form of soot or pitch, or it may be obtained from a decomposable hydrocarbon. The titanium is left in a form capable of recombining with carbon, and thus the process is continuous. The alkali metals give rise to cyanides only; barium yields a mixture of cyanide and cyanamide, whereas calcium cyanamide is the sole product when lime is employed. G. T. M.

Preparation of Aminodicyanodiamidine. TEMISTOCLE JONA (*Gazzetta*, 1908, **38**, ii, 480—484).—Thiele and Uhlfelder's method of preparing aminodicyanodiamidine by nitrating dicyanodiamidine and subsequently reducing (Abstr., 1899, i, 119) gives low yields. As much as 80% of the theoretical quantity can be obtained by reducing nitrodicyanodiamidine by means of hydrochloric acid (D 1·19) and zinc dust at a temperature not higher than 45°. When aminodicyanodiamidine dihydrochloride is heated with *p*-aminobenzaldehyde in a solution faintly acid by hydrochloric acid, it yields a red *compound*, crystallising from alcohol in long filaments and softening at 300° without showing signs of melting; the constitution of this compound is being investigated. T. H. P.

Desmotropy and Fluorescence of Ethyl Oxalosuccinonitrile.

WILHELM WISLICENUS and PAUL BERG (*Ber.*, 1908, **41**, 3757—3768).—Ethyl oxalate (1 mol.) and succinonitrile (1 mol.) condense under the influence of sodium ethoxide, yielding the sodium derivative of ethyl oxalosuccinonitrile, $CN\cdot CH_2\cdot CH(CN)\cdot CO\cdot CO_2Et$. Attempts to bring about condensation with a second molecule of ethyl oxalate were unsuccessful, although succinonitrile condenses with 2 mols. of methyl oxalate; the methyl analogue of the ethyl compound mentioned above could not, however, be prepared. Ethyl oxalosuccinonitrile exists in two tautomeric forms; the enolic form is obtained by treating the sodium derivative with acid, and passes into the ketonic form when warmed in aqueous solution. The ketonic form dissolves in alcohol, forming a bluish-violet, fluorescent solution. This is the first fluorescent substance of the aliphatic series to be prepared, and is consequently of some importance in connexion with the question of the relationship between chemical constitution and fluorescence.

The chemical behaviour of the ketone is represented by the formula $CN\cdot CH_2\cdot CH(CN)\cdot CO\cdot CO_2Et$ with but one exception, namely, its behaviour towards phenylhydrazine; although the enolic form yields a normal phenylhydrazone, the ketonic form gives rise to only small quantities of indefinite substances.

a-Ethyl oxalosuccinonitrile (enolic form),

$$CN\cdot CH_2\cdot C(CN)\colon C(OH)\cdot CO_2Et,$$

crystallises in colourless, pointed leaflets, m. p. 102—103°. The alcoholic solution is not fluorescent, and gives a dark cherry-red coloration with ferric chloride; the *copper* salt, $(C_8H_7O_3N_2)_2Cu$, forms emerald-green, rhombic leaflets, m. p. 118—121° (decomp.). It yields with phenylcarbimide at the ordinary temperature the *additive* product, $CN\cdot CH_2\cdot C(CN)\colon C(O\cdot CO\cdot NHPh)\cdot CO_2Et$, small, flat needles, decomposing at 200°; with ammonia in ethereal solution, the *ammonium* salt, $C_8H_{11}O_3N_3$, long leaflets, decomposing at 145—150°; with phenylhydrazine in alcoholic solution, the *phenylhydrazone*, $C_{14}H_{14}O_2N_4$, colourless needles, m. p. 150—151°; the p-*bromophenylhydrazone*,

$$C_{14}H_{13}O_2N_4Br,$$

has m. p. 181—182°; the *semicarbazone*,

$$CN\cdot CH_2\cdot CH(CN)\cdot C(CO_2Et)\colon N\cdot NH\cdot CO\cdot NH_2,$$

forms long, colourless needles, m. p. 162°; the *oxime*,

$$CN\cdot CH_2\cdot CH(CN)\cdot C(CO_2Et)\colon NOH,$$

crystallises in long needles, m. p. 110°.

β-Ethyl oxalosuccinonitrile (ketonic form) crystallises in pale yellow, microscopic needles, m. p. 154—155°; it is reconverted into the a-form by an alcoholic solution of sodium ethoxide. It does not react with ammonia, *p*-bromophenylhydrazine, semicarbazide hydrochloride, hydroxylamine, or phenylcarbimide at the ordinary temperature, and yields with phenylhydrazine very small quantities of a *substance*, which crystallises in small, golden-yellow needles, decomposing at 122—125°. It reacts with phenylcarbimide at 100°, yielding the additive product described above, and with *p*-bromophenylhydrazine at 100°, forming *oxalic acid di*-p-*bromophenylhydrazide*,

$$C_2O_2(N_2H_2{\cdot}C_6H_4Br)_2,$$

colourless scales, m. p. 240° (decomp.).

Dimethyl dioxalosuccinonitrile,

$$CO_2Me{\cdot}CO{\cdot}CH(CN){\cdot}CH(CN){\cdot}CO{\cdot}CO_2Me,$$

crystallises in yellow, glistening, hexagonal leaflets, m. p. 185°. It does not give a coloration with ferric chloride, but with copper acetate forms a *copper* salt, $(C_{10}H_7O_6N_2)_2Cu$, crystallising in yellowish-green, microscopic needles. W. H. G.

Negative Substituted Amino-oximes. III. Brominated Amino-oximes. WILHELM STEINKOPF and H. GRÜNUPP (*Ber.*, 1908, **41**, 3569—3571).—The authors have prepared the mono-, di-, and tribromoethenylamino-oximes, and have found that, whilst the mono- and di-bromo-compounds resemble in their stability the chloro- and iodo-substituted ethenylamino-oximes, the tribromo-compound is comparatively unstable. The brominated ethenylamino-oximes are prepared by the action of hydroxylamine on the corresponding brominated acetonitriles in the same manner as are the chloro- and iodo-compounds. They give characteristic brown to brownish-red colorations with ferric chloride, and form hydrochlorides when treated with hydrogen chloride in ethereal solution.

Bromoethenylamino-oxime, $CH_2Br{\cdot}C(NOH){\cdot}NH_2$, crystallises in yellowish-white leaflets, m. p. 95—96°, yields a dirty-green precipitate with alkaline copper sulphate solution, and reduces boiling alkaline mercuric chloride.

Dibromoethenylamino-oxime, $CHBr_2{\cdot}C(NOH){\cdot}NH_2$, crystallises in white needles, m. p. 120°, forms a dirty-green precipitate with alkaline copper sulphate, and reduces mercuric chloride in boiling alkaline solution. The *hydrochloride*, white powder, m. p. 163—165° (decomp.).

Tribromethenylamino-oxime, $CBr_3{\cdot}C(NOH){\cdot}NH_2$, m. p. 126°, gradually decomposes at the ordinary temperature. G. Y.

Silicoiodoform. OTTO RUFF [in part, EMIL GEISEL] (*Ber.*, 1908, **41**, 3738—3744).—Silicoiodoform may be obtained in fairly large quantities by the action of hydrogen iodide on siliconitrogen hydride, SiNH, suspended in cold carbon disulphide, or more readily by treating trianilinosilicon hydride, $SiH(NHPh)_3$, with hydrogen iodide in benzene.

Silicoiodoform decomposes slowly above 150°, liberating hydrogen and probably a volatile iodosilicon hydride. The b. p. of silicoiodoform is about 220°/760 mm., but on continued boiling the temperature slowly rises to about 300°; the residue left after distillation is chiefly silicon tetraiodide. Silicoiodoform boils without decomposition under a pressure of 14, 22, 67, and 122 mm. at 106°, 111°, 132°, and 155° respectively; it has D^{23} 3·286.

Trianilinosilicon hydride (*trianilinosilicane*), $SiH(NHPh)_3$, prepared by the interaction of aniline and silicochloroform in benzene, crystallises in slender, white needles, and begins to decompose at 114°. It is converted by hydrogen chloride, bromide, or iodide into the corresponding trihalogenated silicane, and by water into silicoformic acid and aniline.

Siliconitrogen hydride, SiNH, is obtained together with siliconamide by the interaction of siliconchloroform vapour and ammonia diluted with hydrogen at about – 10°, as a white powder. W. H. G.

Silico-acids and their Derivatives. WILHELM MELZER (*Ber.*, 1908, **41**, 3390—3395).—Silicon tetrachloride reacts with organo-magnesium halides, yielding compounds of the type $RSiCl_3$ (compare Kipping, Trans., 1907, **91**, 209), alkyltrichlorosilicanes. These react with water, yielding the silico-acids, $R\cdot SiO_2H$, and with anhydrous alcohol, yielding the ortho-esters, $R\cdot Si(OEt)_3$. In the preparation of the chlorides, it is essential that all traces of moisture should be removed.

Propyltrichlorosilicane, $C_3H_7\cdot SiCl_3$, is a clear, colourless liquid, b. p. 123—125°; it has a penetrating odour, and fumes in contact with the air.

Silicobutyric acid, $C_3H_7\cdot SiO_2H$, forms a hard, solid mass, which can be ground to a powder. It is infusible.

Ethyl orthosilicobutyrate, $C_3H_7\cdot Si(OEt)_3$, is a colourless liquid with an aromatic odour, and has b. p. 177—179° and D 0·8945.

iso*Amyltrichlorosilicane*, $C_5H_{11}\cdot SiCl_3$, is a colourless liquid, b. p. 46°/9 mm., D 1·066.

Ethyl orthosilicohexoate, $C_5H_{11}\cdot Si(OEt)_3$, has b. p. 195—200° and D 0·9318.

Silicohexoic acid, $C_5H_{11}\cdot SiO_2H$, forms a hard, brittle solid, soluble in ether, benzene, or chloroform, and has not a definite m. p.

Benzyltrichlorosilicane, $C_6H_5\cdot CH_2\cdot SiCl_3$, has b. p. 94—96°/11 mm. and D 1·2834. The *ortho*-ester, $C_6H_5\cdot CH_2\cdot Si(OEt)_3$, has b. p. 245—250° and D 0·9864. *Silicophenylacetic acid*, $C_6H_5\cdot CH_2\cdot SiO_2H$, separates from ether as a clear, vitreous solid, m. p. 65—66°.

a-Naphthyltrichlorosilicane, $C_{10}H_7\cdot SiCl_3$, is a viscid liquid with a penetrating odour, and has b. p. 165—170°/22 mm. and D 1·3760. The *ortho*-ester, $C_{10}H_7\cdot Si(OEt)_3$, has b. p. 220—230°/18 mm., and the *acid*, $C_{10}H_7\cdot SiO_2H$, has m. p. 125—130° (compare Khotinsky and Seregenkoff, this vol., i, 1032). J. J. S.

Velocity of Decomposition of the Ozonides of Certain Cyclic Hydrocarbons. CARL D. HARRIES and HANS VON SPLAWA NEYMANN (*Ber.*, 1908, **41**, 3552—3558).—In the communication of Harries and Neresheimer (Abstr., 1906, i, 833), it is incorrectly stated that a sparingly soluble ozonide of *cyclo*hexene is obtained by passing ozone into a solution of the hydrocarbon in chloroform. This ozonide is formed when carbon tetrachloride is the solvent, whilst when chloroform or hexane is the solvent employed, an ozonide is obtained which may be crystallised from alcohol. The two ozonides have approximately the same composition, and behave similarly when decomposed by water.

The decomposition of the ozonides of *cyclo*pentene and *cyclo*hexene by water has been studied quantitatively (compare Harries and Tank, this vol., i, 517); it is found that under similar conditions *cyclo*pentene ozonide is decomposed in one hour to about the same extent as *cyclo*hexene ozonide in two and a-half hours.

α-cyclo*Hexene ozonide*, $C_6H_{10}O_3$, obtained by passing ozone into a solution of the unsaturated hydrocarbon in hexane, crystallises in stellate groups of small, white needles, m. p. 75°; it decomposes at 90°.

β-cyclo*Hexene ozonide* is formed together with the α-ozonide by acting on a solution of the hydrocarbon in carbon tetrachloride with ozone; it is a sparingly soluble, solid substance, m. p. 115—120° (decomp.), and when analysed gives values which lie between those required for $C_6H_{10}O_3$ and $C_6H_{10}O_4$.

Both ozonides are decomposed by boiling water, yielding adipic acid (about 44%), adipic dialdehyde, *cyclo*pentenealdehyde, and adipic semialdehyde (about 13%). *Adipic semialdehyde* (*δ-aldehydovaleric acid*), $CHO\cdot[CH_2]_4\cdot CO_2H$, forms colourless crystals, m. p. 124—125°; the p-*nitrophenylhydrazone* crystallises in yellow needles, m. p. 134°.

W. H. G.

Lowest Oxides of Hydrogen Sulphide. EMIL FROMM (*Ber.*, 1908, 41, 3397—3425).—[With ADOLF ROESICKE.]—In previous communications (Abstr., 1906, i, 656; 1907, i, 982; this vol., i, 700), the author has stated the rule that organic disulphides of the type

$$X:CR\cdot S\cdot S\cdot CR_1:Y,$$

containing neighbouring double linkings, are decomposed by water or alkalis, sulphur being eliminated. An attempt has been made to apply the rule to the elucidation of the constitution of sodium tetrathionate. If this salt be represented as $ONa\cdot SO_2\cdot S\cdot S\cdot SO_2\cdot ONa$, its decomposition by water should be as follows:

$$\text{I. } ONa\cdot SO_2\cdot S\cdot S\cdot SO_2\cdot ONa + H_2O = ONa\cdot SO_2\cdot SH + S + HO\cdot SO_2\cdot ONa.$$

$$\text{II. } ONa\cdot SO_2\cdot SH + HO\cdot SO_2\cdot ONa = Na_2SO_4 + S + SO_2 + H_2O.$$

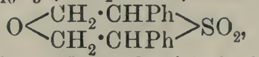
The amounts of sulphur and of sodium sulphate (compare Gutmann, Abstr., 1907, ii, 862) obtained when sodium tetrathionate and water are repeatedly evaporated to dryness approximate to the quantities required by the preceding equations. Experiments, in which the prevention of the secondary reaction is attempted by the addition of ammonium hydroxide or sodium hydrogen carbonate, do not give satisfactory results. In the decomposition of sodium tetrathionate by water or alkalis, it seems impossible to stop secondary reactions, but there appears to be no doubt that sulphur is always a product of the primary reaction.

Aromatic disulphides are exceptions to the foregoing rule; by treatment with an alkali, they are decomposed without elimination of sulphur. The author regards the decomposition as occurring initially, thus: $Ph\cdot S\cdot S\cdot Ph + H_2O = Ph\cdot SH + Ph\cdot S\cdot OH$, but the evidence for this view is by no means conclusive. When phenyl disulphide, alcoholic sodium hydroxide, and benzyl chloride are heated in a reflux apparatus, *phenyl benzyl sulphide*, $Ph\cdot S\cdot CH_2Ph$, m. p. 42°, and phenylbenzylsulphone are obtained, without doubt by the action of the benzyl chloride on the initially formed phenyl mercaptan and benzenesulphinic acid respectively (compare Schiller and Otto, this Journ., 1877, 463). Since, however, benzoic acid is also formed from the benzyl chloride when 4 : 4′-dinitrodiphenyl disulphide is used in the place of phenyl disulphide (this vol., i, 631), some oxidising agent must be produced in the reaction; this fact furnishes the chief evidence for the author's view quoted above. The hypothetical phenyl derivative of sulphur hydrate, Ph·S·OH, being unstable in alkaline solution, changes to phenyl mercaptan and benzenesulphinic acid, somewhat like benzaldehyde in the Cannizzaro reaction. By the decomposition of sodium ethyl thiosulphate by alcoholic sodium hydroxide, Gutmann (Abstr., 1907, i, 671; this vol., i, 497) obtained a solution which oxidised arsenites to arsenates, and probably contained the ethyl derivative, Et·S·OH. By treating this solution with benzyl chloride, the author obtains ethyl mercaptan, benzyl ethyl sulphide, benzylethylsulphone, and benzyl disulphide; the formation of these substances is regarded as furnishing additional evidence for the existence of the ethyl derivative of sulphur hydrate. The fission of *p*-tolyl disulphoxide by sodium hydroxide in the presence of benzyl chloride yields *p*-toluenesulphinic acid, *p*-tolyl disulphide, and *p*-tolylbenzylsulphone, the formation of which is due to the action of the benzyl chloride on the sulphinic acid (compare Otto and Rossing, Abstr., 1886, 711; Remsen and Turner, Abstr., 1901, i, 270; Fromm and Palma, Abstr., 1906, i, 819).

[With O. Gaupp.]—Derivatives of sulphoxylic acid, H_2SO_2, have been obtained by several investigators (compare Bazlen, Abstr., 1905, ii, 240; Reinking, Dehnel, and Labhardt, *ibid.*, i, 261). By the interaction of zinc dust and sulphuryl chloride in dry ether, Fromm and Palma (Abstr., 1906, i, 819) obtained a solution of zinc sulphoxylate, which yielded dibenzylsulphone by heating with benzyl chloride and 10% sodium hydroxide. A more searching examination of the reaction has shown the presence of a small amount of benzylsulphonic acid, so that the formation of zinc hyposulphite in the first reaction is not excluded, as previously mentioned. Since, however, sodium or zinc hyposulphite is insoluble in dry ether, or in ether containing water, alcohol, or zinc chloride, the formation of the sulphonic acid cannot be due to a hyposulphite; its production is explained thus: (I) $Zn + SO_2Cl_2 = ZnCl_2 + SO_2$. (II) $SO_2 + 2NaOH + CH_2PhCl = NaCl + CH_2Ph{\cdot}SO_3Na + H_2O$. Magnesium, copper, iron, or sodium have no action on sulphuryl chloride in dry ether, but sodium amalgam reacts vigorously, the product yielding with benzyl chloride and sodium hydroxide, benzylsulphonic acid, the formation of which is again attributed to the liberation of sulphur dioxide.

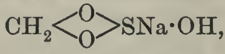
Aldehydes or ketones react with sodium hyposulphite in the presence of sodium hydroxide in accordance with the equation: $RR'CO + Na_2S_2O_4 + NaOH = RR'C(OH){\cdot}SO_2Na + Na_2SO_3$ (compare Meister, Lucius & Brüning, Eng. Pat., 1903, 5867; *Chem. Zentr.*, 1906, i, 423; Bazlen, *loc. cit.*). The substance, $RR'C(OH){\cdot}SO_2Na$, may be a hydroxysulphinate, an ester of sodium hydrogen sulphoxylate, or a derivative of orthosulphoxylic acid (compare Bazlen, *loc. cit.*). To ascertain which representation is correct, the behaviour of Rongalite *C* (sodium formaldehydesulphoxylate), $OH{\cdot}CH_2{\cdot}SO_2Na$, has been studied. The reduction of rongalite by tin and hydrochloric acid, or by hydrogen sulphide in the presence of hydrochloric acid, does not give much information, since the production of the substance obtained, trithioformaldehyde, is explicable by each formula. Oxidation by potassium permanganate, or by chlorine or bromine water, causes complete decomposition. Better results are obtained by adding an alcoholic solution of benzyl chloride to rongalite and aqueous sodium hydroxide, and heating for three hours, whereby dibenzylsulphone, sodium benzylsulphonate in small amount, and *dibenzylrongalite*, $C_{15}H_{16}O_3S$, m. p. 80—81°, are obtained; in the absence of the alkali, only the sulphone is formed. The formation of the sulphone in the presence or the absence of sodium hydroxide is evidence for the sulphoxylate formula of rongalite: (I) $OH{\cdot}CH_2{\cdot}O{\cdot}SO{\cdot}Na + NaOH + 2C_7H_7Cl = SO_2(C_7H_7)_2 + 2NaCl + CH_2O + H_2O$. (II) $OH{\cdot}CH_2{\cdot}O{\cdot}SO{\cdot}Na + 2C_7H_7Cl = SO_2(C_7H_7)_2 + NaCl + HCl + CH_2O$.

Dibenzylrongalite is not formed in a secondary reaction between dibenzylsulphone, sodium hydroxide, and rongalite, neither does it yield the sulphone by heating with sodium hydroxide in the presence or the absence of benzyl chloride. Its formation is not due to a reaction between dibenzylsulphone and formaldehyde, for these two substances, heated with 10% sodium hydroxide, form *diformaldibenzylsulphone*, $C_{16}H_{16}O_3S$, m. p. 188°, which from its behaviour receives the constitution



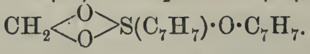
$O{<}\begin{matrix}CH_2{\cdot}CHPh\\CH_2{\cdot}CHPh\end{matrix}{>}SO_2$,

and is not obtained from dibenzylrongalite. Treated with hydrogen chloride in glacial acetic acid, dibenzylrongalite yields benzyl chloride (hence one benzyl group is attached to oxygen) and *formaldibenzyldisulphoxide*, $C_{15}H_{14}O_2S_2$, m. p. 108°; the latter is also obtained from dibenzyl disulphoxide, $C_{14}H_{14}O_2S_2$, m. p. 108°, formaldehyde, and hydrogen chloride. Dibenzylrongalite is decomposed by bromine in chloroform in sunlight, yielding benzyl bromide, *benzylsulphonyl bromide*, $C_7H_7{\cdot}SO_2Br$, m. p. 79°, and *p*-bromobenzylsulphonic acid. Reviewing the preceding decompositions, the author concludes that rongalite is a sulphoxylate, $OH{\cdot}CH_2{\cdot}O{\cdot}SO{\cdot}Na$ or



$CH_2{<}\begin{matrix}O\\O\end{matrix}{>}SNa{\cdot}OH$,

and that dibenzylrongalite has the constitution $C_7H_7{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}SO{\cdot}C_7H_7$ or



$$CH_2{<}\begin{matrix}O\\O\end{matrix}{>}S(C_7H_7){\cdot}O{\cdot}C_7H_7.$$

Sodium acetonesulphoxylate is more stable than rongalite, for a substance analogous to dibenzylrongalite is not obtained when its solution is heated with benzyl chloride and sodium hydroxide. Since, also, sodium benzaldehydesulphoxylate (Bazlen, *loc. cit.*) is unchanged when heated at 120° with benzyl chloride and aqueous sodium hydroxide, the author ascribes to these two sulphoxylates the formulæ of hydroxysulphinates: $OH{\cdot}CMe_2{\cdot}SO_2Na$ and $OH{\cdot}CHPh{\cdot}SO_2Na$.

C. S.

Preparation of Sulphinic Acids. EMIL KNOEVENAGEL and JAMES KENNER (*Ber.*, 1908, **41**, 3315—3322).—The authors find that aromatic sulphinic acids can be readily prepared in a yield of about 80% by the action (first studied by Friedel and Crafts, Abstr., 1890, 241) of sulphur dioxide and aluminium chloride on aromatic hydrocarbons or their halogen derivatives at a low temperature. The reaction is started by passing dry hydrogen chloride through the mixture, and the compound of aluminium chloride and aromatic sulphinic acid is decomposed by alkalis. Phenol ethers also yield sulphinic acids very readily, and the use of hydrogen chloride is not necessary, but sulphoxides and sulphonium compounds are also produced. The reaction is probably accompanied by the intermediate formation of the compound $AlCl_2\cdot SO_2Cl$.

Sulphinic acids were prepared from benzene, *p*-toluene, *o*-, *m*-, and *p*-xylene, mesitylene (m. p. 100°. Holtmeyer, *Zeitsch. Chem.*, 1867, 686, gives 98—99°), *ψ*-cumene, *p*-cymene, naphthalene (α-acid), *p*-chlorobenzene (m. p. 98—99°. Oberländer, *Diss.*, Heidelberg, gives 5° lower), and *p*-bromobenzene.

Anisole yields anisolesulphinic acid (m. p. 73°. Kreuder, *Diss.*, Heidelberg, gives 97—98°) together with di-*p*-anisyl sulphoxide and trianisylsulphonium chloride (isolated as platinichloride). From phenetole a mixture of the sulphoxide and sulphonium compound was obtained. J. C. C.

Sulphinic Anhydrides. Emil Knoevenagel and Leo Polack (*Ber.*, 1908, **41**, 3323—3331).—When aromatic sulphinic acids are treated in the cold with acetic anhydride and a drop of concentrated sulphuric acid, or a few drops of a 0·1% solution of ferric chloride in acetic acid or acetic anhydride, the corresponding sulphinic anhydrides are produced.

Benzenesulphinic anhydride, $O(SO\cdot C_6H_5)_2$ (probably previously obtained by Otto and Ostrop, *Annalen*, 1866, **141**, 374, as an oil; compare also Otto and Gruber, *ibid.*, 1868, **145**, 11), is a white, crystalline substance, m. p. 66—67°. When preserved in a closed vessel or over concentrated sulphuric acid in a vacuum desiccator, it decomposes with the formation of benzene disulphoxide, $C_6H_5\cdot SO_2\cdot S\cdot C_6H_5$, and benzenesulphonic acid, together with compounds of high m. p. The latter are not formed when the substance is kept in a vacuum desiccator over soda-lime, and the above decomposition proceeds more slowly.

Toluene-p-*sulphinic anhydride*, $C_6H_4Me\cdot SO\cdot O\cdot SO\cdot C_6H_4Me$, has m. p. 75°; it decomposes after a time into *p*-toluene disulphoxide and a mixture of toluene-sulphinic and -sulphonic acids.

p-*Xylenesulphinic anhydride*, $O(SO\cdot C_6H_3Me_2)_2$, has m. p. 68—69°. In a vacuum desiccator it decomposes into *p*-xylenesulphonic acid and p-*xylene disulphoxide*, white tablets, m. p. 70—72°. The same products are formed when *p*-xylenesulphonic acid is heated in a sealed tube at 120—130°.

ψ-Cumenesulphinic anhydride, $O(SO\cdot C_6H_2Me_3)_2$, has m. p. 92—93°. *Mesitylenesulphinic anhydride* has m. p. 118—121°. p-*Cymenesulphinic anhydride* was obtained as an oil, which was probably a mixture of isomerides. p-*Bromobenzenesulphinic anhydride* begins to melt at 79—81°, and is completely molten at 108—109°. Even after ten minutes the m. p. is raised to 140°, and after a longer time the substance is converted into p-*bromobenzene disulphoxide*, m. p. 155·5°, which is also formed on heating *p*-bromobenzenesulphinic acid in a sealed tube at 120—130°. p-*Iodobenzenesulphinic anhydride*, when freshly prepared, begins to melt at 75—80°, and is completely molten above 100°. After half an hour the m. p. is 160° (decomp.), and *p*-iodobenzene disulphoxide is probably present.

When benzene- or *p*-toluene-sulphinic anhydride is mixed with ammonium carbonate, the ammonium salt of the corresponding sulphonic acid is formed, together with the corresponding disulphoxide. The latter anhydride gives with dry ammonia, ammonium toluene-*p*-sulphonate, together with the corresponding disulphoxide and a trace of the sulphinic acid. When the experiment is carried on after the vessel containing the toluene-*p*-sulphinic anhydride has been filled with dry hydrogen, a small amount of *p*-toluenesulphonamide is formed. Benzenesulphonic anhydride gives with diethylamine the diethylamine salt of benzenesulphinic acid; with aniline, di-*p*-aminophenyl sulphoxide; with *p*-toluidine, the corresponding salt of benzenesulphinic acid, and with phenol, hydroxydiphenyl sulphide. J. C. C.

Action of Arsenites and Cyanides on Thiosulphonates. August Gutmann (*Ber.*, 1908, **41**, 3351—3356).—Sodium toluene-*p*-thiosulphonate is reduced by potassium cyanide or sodium arsenite in sodium hydroxide solution to the *p*-sulphinate, with attendant formation of thiocyanate or thioarsenate at 100°: $C_6H_4Me{\cdot}S_2O_2Na + Na_3AsO_3 = C_6H_4Me{\cdot}SO_2Na + Na_3AsO_3S$.

A solution of the toluene-*p*-thiosulphonate, boiled with 10 mols. of sodium hydroxide in 15% solution, becomes lemon-yellow, and on evaporation deposits sulphinate. The yellow solution gives with hydrochloric acid, sulphur and sulphinate, but no hydrogen sulphide; with an alkaline zinc solution, no zinc sulphide, and with arsenite or cyanide, decolorisation at once results. The conclusion is drawn that the yellow colour is due to NaOSH, the *sodium hydropersulphide* reacting thus with cyanide: $NaOSH + KCN = KCNS + NaOH$.

Sodium sulphide also gives a deep yellow solution, which is likewise decolorised by cyanide or arsenite, and is held to contain NaSSH.

W. R.

Transposition of Phenyl. Migration of the Naphthyl Group in Iodohydrins of the Naphthalene Series. Marc Tiffeneau and Daudel (*Compt. rend.*, 1908, **147**, 678—680).—The authors find that, exactly as in the cases previously observed with the phenyl group (compare this vol., i, 165, 166), the naphthyl nucleus in derivatives containing the ethylene linking migrates under the influence of iodine and mercuric oxide, thus:

$$Ar{\cdot}CH(OH){\cdot}CHI{\cdot}CH_3 \longrightarrow CHO{\cdot}CHAr{\cdot}CH_3$$
$$Ar{\cdot}CMe(OH){\cdot}CH_2I \longrightarrow CH_3{\cdot}CO{\cdot}CH_2Ar.$$

a-Allylnaphthalene, $C_{10}H_7{\cdot}CH_2{\cdot}CH{:}CH_2$, prepared by the interaction of allyl bromide and magnesium α-naphthyl bromide, has b. p. 265—267°; with mercuric oxide and iodine in aqueous ethereal solution, the *iodohydrin*, $C_{10}H_7{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2I$, is obtained, which loses its iodine when treated with silver nitrate, but the aldehydic compound is not formed.

a-Naphthylpropylene, $C_{10}H_7{\cdot}CH{:}CH{\cdot}CH_3$, produced by boiling *a*-allylnaphthalene with alcoholic potassium hydroxide, has b. p. 147—149°/15 mm., and 275—278° under the ordinary pressure, accompanied by partial polymerisation. When treated with mercuric oxide and iodine, it is directly transformed into α-1-naphthylpropaldehyde, b. p. 170—171°/14 mm., D^0 1·118 (Darzens, this vol., i, 91), which, on oxidation, yields α-1-*naphthylpropionic acid*, m. p. 145°.

β-1-*Naphthylpropylene*, $C_{10}H_7{\cdot}CMe{:}CH_2$, with iodine and mercuric oxide, gives *α-naphthylacetone*, $C_{10}H_7{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, the *semicarbazone* of which has m. p. 205°.

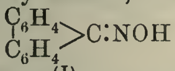
α-Naphthylethylene, $C_{10}H_7{\cdot}CH{:}CH_2$, prepared by the interaction of acetaldehyde and magnesium α-naphthyl bromide, is the chief constituent of the fraction of the products, b. p. 135—138°/15 mm.; with iodine and mercuric oxide, it yields *α-naphthylacetaldehyde*,

$$C_{10}H_7{\cdot}CH_2{\cdot}CHO,$$

b. p. 163—166°/13 mm. The *semicarbazone* has m. p. 208°. On oxidation, the aldehyde yields α-naphthylacetic acid. J. C. C.

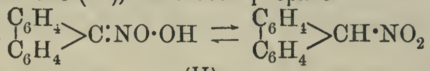
Condensation of Fluorene with Alkyl Nitrites and Nitrates by means of Potassium Ethoxide.

Wilhelm Wislicenus and Martin Waldmüller (*Ber.*, 1908, 41, 3334—3340).—Although fluorene does not react with amyl nitrite (Thiele and Henle, Abstr., 1906, i, 571) or ethyl nitrate (Wieland, *Diss.*, Munich, 1901) in presence of sodium ethoxide, the authors find that the condensation proceeds smoothly when potassium ethoxide is used. From fluorene and amyl nitrite, fluorenoneoxime (I), and from fluorene and ethyl nitrate, 9-nitrofluorene (II), have been prepared.



$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C{:}NOH$$

(I).

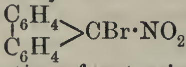


$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C{:}NO{\cdot}OH \rightleftharpoons \begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>CH{\cdot}NO_2$$

(II).

The two desmotropic forms of the latter have been obtained; the *aci*-form is comparatively very stable. For the condensation, an alcoholic-ethereal solution of potassium ethoxide is used.

The *potassium* compound of fluorenoneoxime, $C(C_6H_4)_2{:}NOK$, is stable in dry air, and decomposes between 210° and 220°. With water it yields fluorenoneoxime.

The *potassium* compound of 9-*iso*nitrofluorene (9-*aci*-nitrofluorene) results from the condensation of fluorene and ethyl nitrate in presence of potassium ethoxide. It forms small, yellow needles, and a dilute solution of it gives a dark green coloration with ferric chloride. The corresponding *ammonium* salt, small, yellow crystals, decomposing at 146—148°, *sodium* salt, glistening, yellow leaflets, and *silver* salt are described. 9-iso*Nitrofluorene* (9-aci-*nitrofluorene*), prepared from the sodium salt, forms small, greenish-yellow needles, m. p. 132—135°; it dissolves in potassium hydroxide. 9-Nitrofluorene, formed when an alcoholic solution of the *aci*-compound is kept or is warmed for a short time, crystallises in small, colourless, glistening tablets, m. p. 181—182° (decomp.). It is insoluble in potassium hydroxide, but is dissolved by sodium or potassium ethoxide, regenerating the *aci*-form. An ethereal solution of the *aci*-form gives with dry ammonia an immediate precipitate of the ammonium salt, but the true nitro-compound does not react with ammonia under the same conditions. Phenylcarbimide is without action on the nitro-derivative, whilst with the *aci*-form a vigorous reaction ensues, accompanied by evolution of gas. Both forms of nitrofluorene yield fluorenone when carefully heated. When a solution of the potassium compound of the *aci*-form is exposed to the air, or if air is passed through the solution, fluorenone and potassium nitrite are formed; the reaction proceeds more quickly with an absolute alcoholic solution. 9-*Bromo*-9-*nitrofluorene*,  $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}>CBr{\cdot}NO_2$, prepared by adding bromine water to an aqueous solution of potassium *aci*-nitrofluorene, forms small, yellow, glistening needles, m. p. 107—108° (decomp.). On heating, bromine and nitrogen dioxide are evolved and fluorenone is formed. J. C. C.

Hydrofluorides of Some, in Part very Weak, Organic Bases. RUDOLF F. WEINLAND and F. REISCHLE (*Ber.*, 1908, **41**, 3671—3674. Compare Weinland and Lewkowitz, Abstr., 1905, i, 518).—The following hydrofluorides have been prepared: From triphenylamine (with concentrated alcoholic hydrofluoric acid), NPh_3,HF, bright green powder; from diphenylamine, with aqueous hydrofluoric acid,

$$NHPh_2,2HF,$$

small, colourless crystals; with alcoholic hydrofluoric acid,

$$NHPh_2,3HF,$$

colourless leaflets; from azobenzene, N_2Ph_2,HF, long, orange-red, glistening needles; from dimethylpyrone, with aqueous hydrofluoric acid, $C_7H_8O_2,3HF,\frac{1}{2}H_2O$, large, colourless prisms, and with alcoholic hydrofluoric acid, $C_7H_8O_2,3\frac{1}{2}HF,\frac{1}{2}H_2O$, leaflets. J. C. C.

Studies in Nitration. V. Melting Points of Mixtures of *o*- and *p*-Nitroanilines. J. BISHOP TINGLE and H. F. ROLKER (*J. Amer. Chem. Soc.*, 1908, **30**, 1764—1767. Compare Abstr., 1907, i, 120; this vol., i, 408, 778, 893).—In an earlier paper (this vol., i, 408), the melting points of mixtures of *o*- and *m*-, and of *m*- and *p*-nitroanilines were recorded, and it was stated that the curve for mixtures of the ortho- and para-compounds was very irregular. The experiments on *o*- and *p*-nitroaniline have now been repeated, in which the difference in composition between consecutive mixtures was 2%. Curves have been constructed showing the melting points of the original mixtures and the melting points after the fused mixtures had been cooled quickly and then re-melted. It is suggested that the variations in these two series of melting points are due to polymorphism, a substance on melting changing into another form with a different m. p.

The solubility of the nitroanilines in alcohol has been determined. At 15°, 100 c.c. of 95% alcohol dissolve 15·848 grams of *o*-, 4·960 grams of *m*-, and 4·030 grams of *p*-nitroaniline. E. G.

ω-Chloroacetanilide and Some Halogenphenylglycines. CARL G. SCHWALBE, W. SCHULZ, and HERMANN JOCHHEIM (*Ber.*, 1908, **41**, 3790—3796).—It is known that the presence of negative groups makes the displacement of a halogen in a benzene derivative more easily effected. It was therefore anticipated that oxindole would be formed on heating *o*-ω-dichloroacetanilide with copper powder, and that indigotin would result from the fusion of *o*-chlorophenylglycine with sodamide.

The halogen is, however, too firmly held, and only a 0·4% yield of indigotin was obtained, and oxindole could only be detected.

o-ω-Dichloroacetanilide, $C_6H_4Cl{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$, prepared either from chloroacetic acid, *o*-chloroaniline, and phosphorus trichloride (compare Janson, Abstr., 1907, i, 312), or from chloroacetyl chloride and *o*-chloroaniline, crystallises from light petroleum in woolly needles, m. p. 67°.

o-Chlorophenylglycine, $C_8H_8O_2NCl$, obtained from *o*-chloroaniline by heating with alcoholic potash, formaldehyde, and potassium cyanide (Abstr., 1904, i, 153), crystallises in white leaflets, m. p. 171°. The *amide*, $C_8H_9ON_2Cl$, forms white, glistening needles, m. p. 142°; the *ethyl* ester, $C_{10}H_{12}O_2NCl$, is a colourless oil, b. p. 288—291°; *acetyl-o-chlorophenylglycine*, $C_{10}H_{10}O_3NCl$, forms white crystals, decomp. 210°; its *ethyl* ester, $C_{12}H_{14}O_3NCl$, is a colourless liquid, b. p. 205°/20 mm. The m- and p-*chlorophenylglycines* have m. p.'s 93° and 141° respectively; 2 : 4-*dichlorophenylglycine*, $C_8H_7O_2NCl_2$, crystallises from water; m. p. 127°. The o- and p-*bromophenylglycines*, $C_8H_8O_2NBr$, have m. p.'s 157° and 150°. W. R.

Preparation of Aromatic Glycines. GEORGES IMBERT and CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 199624).—Aromatic glycines have hitherto been prepared by the interaction of monohalogenated acetic acids and aromatic amines. It has now been found that the former may be replaced by the dihalogenated vinyl ethers, the latter being supposed to change in the following manner: $C_2HCl_2{\cdot}OEt + H_2O = HCl + CH_2Cl{\cdot}CO_2Et$. Accordingly, 1 mol. of the dihalogenated vinyl ether is allowed to react with 3 mols. of the aromatic base in aqueous or dilute alcoholic solution, but the excess of base may be replaced by some acid-fixing agent, such as calcium, magnesium, or barium carbonate. Ethyl dichloro- or dibromo-vinyl ether and aniline give rise to a mixture of ethyl phenylglycinate (90%) and phenylglycinanilide (10%). G. T. M.

Diphenylamine Derivatives. FRITZ ULLMANN and REINER DAHMEN (*Ber.*, 1908, **41**, 3744—3755).—While attempting to prepare 4-nitrodiphenylamine-2-sulphonic acid by Fischer's method (Abstr., 1892, 331) with the object of obtaining from it the corresponding sulphone by elimination of water, it was found, on boiling the aqueous solution of the acid with a small quantity of sulphuric acid, that the sulpho-group was removed, with the formation of *p*-nitrodiphenylamine. Further investigation has shown that aminodiphenylamine-2-sulphonic acids behave in a similar manner; it has therefore been found possible by this method to prepare the following derivatives of diphenylamine: *p*-nitro-, *p*-amino-, 4-nitro-4′-amino-, 4-nitro-3′-amino-, and 4-nitro-2′-amino-diphenylamine, 4-nitrophenyl-2′-tolylamine, 4-nitrophenyl-4′-tolylamine, and 4-aminophenyl-4′-tolylamine.

The sodium salts of the *o*-sulphonic acids were obtained by the interaction of the base with sodium 2-chloro-5-nitrobenzenesulphonate; in the case of aniline and *o*-toluidine, the condensation was brought about by heating in the presence of calcium carbonate and glycerol; with *p*-toluidine and the three phenylenediamines, the components were simply heated together in aqueous solution with calcium carbonate.

Sodium 4-nitrophenyl-2′-tolylamine-2-sulphonate, $C_{13}H_{11}O_5N_2SNa$, crystallises in yellow needles. 4-*Nitrophenyl-2′-tolylamine*, $C_{13}H_{12}O_2N_2$, forms glistening, dark yellow leaflets, m. p. 115°, and is reduced to 4-*aminophenyl-2′-tolylamine*, $C_{13}H_{14}N_2$, white leaflets, m. p. 58·5°, the *sulphate* of which forms white needles. The *p*-amino-compound may also be obtained from 4-*aminophenyl-2′-tolylamine-2-sulphonic acid*, $C_{13}H_{14}O_3N_2S$, which crystallises in small, colourless needles.

Sodium 4-nitrophenyl-4′-tolylamine-2-sulphonate, $C_{13}H_{11}O_5N_2SNa$, forms orange-red needles with a blue reflex. 4-Nitro-4′-aminodiphenylamine has m. p. 207°: Bandrowski gives m. p. 211° (Abstr., 1901, i, 48); the *hydrochloride*, $C_{12}H_{11}O_2N_3,HCl$, forms dark steel-blue, glittering needles.

4-*Nitro-4′-aminodiphenylamine-2-sulphonic acid*, $C_{12}H_{11}O_5N_3S$, crystallises in yellowish-brown needles.

4-*Nitrophenyl-4′-tolylamine*, $C_{13}H_{12}O_2N_2$, crystallises in glistening, yellow needles, m. p. 136°. 4-*Aminophenyl-4′-tolylamine-2-sulphonic acid*, $C_{13}H_{14}O_3N_2S$, forms small, white needles; the *sodium* salt crystallises in colourless leaflets.

4-*Nitro-3′-aminodiphenylamine-2-sulphonic acid*, $C_{12}H_{11}O_5N_3S$, forms brownish-yellow needles. 4-*Nitro-3′-aminodiphenylamine*, $C_{12}H_{11}O_2N_3$, crystallises in glistening, brownish-yellow leaflets, m. p. 156°; the *hydrochloride* forms large, deep yellow needles with a blue reflex.

4-*Nitro-2′-aminodiphenylamine-2-sulphonic acid*, $C_{12}H_{11}O_5N_3S$, crystallises in yellow needles. It is converted when boiled with dilute sulphuric acid into 4-nitro-2′-aminodiphenylamine (14%) and 4-nitrophenol-2-sulphonic acid.

W. H. G.

Phenyl-, Naphthyl-, and Menthyl-carbimides. C. Vallée (*Ann. Chim. Phys.*, 1908, [viii], 15, 331—432).—The author has made an exhaustive examination of the reactions between certain arylcarbimides and (1) organic acids (compare Abstr., 1905, i, 771), (2) phenol and some of its substituted derivatives, (3) esters of hydroxy-acids, (4) amino-acids, and of the condensation of *s*-diphenylcarbamide with certain acyl tartaric anhydrides. The following compounds are described for the first time: *aniline benzenesulphinate*, $PhSO_2H,NH_2Ph$, m. p. 132°; *aniline hydroxybenzylphosphinite*,

$$OH\cdot CHPh\cdot PHO\cdot OH\cdot NH_2Ph,$$

m. p. 99°; *aniline dihydroxydibenzylphosphinate*,

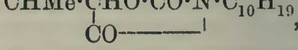
$$PO(CHPh\cdot OH)_2\cdot OH,NH_2Ph,$$

m. p. 190°; the *diphenylurethane* of *ethyl dihydroxydibenzylphosphinate*, $C_{30}H_{29}O_6N_2P$, m. p. 203°; *phenylurethane* of *tribromophenol*,

$$C_6H_2Br_3\cdot O\cdot CO\cdot NHPh,$$

m. p. 168°; *menthylurethane* of *trimethylcarbinol*,

$$CMe_3\cdot O\cdot CO\cdot NH\cdot C_{10}H_{19},$$

m. p. 112°, $[\alpha]_D$ − 55·33° in toluene; the menthylurethane derivative of ethyl lactate yields the *lactam*,  $\underset{\lvert\!\!-\!\!-\!\!-\;CO\;-\!\!-\!\!-\!\!\rvert}{CHMe\cdot CHO\cdot CO\cdot N\cdot C_{10}H_{19}}$, m. p. 77·5°.

The phenylurethanes of substituted phenols, or of the esters of hydroxy-acids, are readily prepared by heating phenylcarbimide with the hydroxy-compound in the presence of a small quantity of sodium; the phenylurethane of methyl tartrate crystallises in the monoclinic system [$a:b:c = 1·0544 : 1 : 0·4566$; $\beta = 103°$].

The influence of (*a*) the solvent, (*b*) the molecular weight and the position of the substituting radicles, and (*c*) the ethylenic linking in the radicles on the specific rotation of the numerous optically active urethanes prepared in the course of the work is fully discussed in the paper. M. A. W.

Preparation of Compounds of *p*-Aminophenol, *p*-Methylaminophenol, and *p*-Phenylenediamine with Sulphurous Acid. SOCIÉTÉ ANONYME DES PLAQUES ET PAPIERS PHOTOGRAPHIQUES A. LUMIÈRE ET SES FILS (D.R.-P. 198497).—Crystalline additive compounds of sulphurous acid with *p*-aminophenol, *p*-methylaminophenol, and *p*-phenylenediamine may be produced either by passing sulphur dioxide into a hot aqueous solution or suspension of these bases, or by treating them with 40% aqueous sodium hydrogen sulphite. The salts of the bases may be employed for this reaction, providing that a mixture of sulphite and hydrogen sulphite is employed.

The *compound*, $10NH_2·C_6H_4·OH,H_2SO_3$, from *p*-aminophenol, white leaflets, m. p. 184°, is only sparingly soluble in cold water.

The *compound*, $6NHMe·C_6H_4·OH,H_2SO_3$, from *p*-methylaminophenol, forms small, colourless, odourless crystals, decomposing at 87°.

The *compound*, $9C_6H_4(NH_2)_2,H_2SO_3$, from *p*-phenylenediamine, colourless crystals, m. p. 137°, has a faint odour of sulphur dioxide; it is readily soluble in cold water. These products find employment as photographic developers. G. T. M.

Abnormal Salts. ANTONI KORCZYŃSKI (*Bull. Acad. Sci. Cracow*, 1908, 633—644).—Finely-powdered phenols and acids have been submitted to the action of dry ammonia. At the ordinary temperature, 1 mol. of ammonia is absorbed by *o*-nitrophenol, 1-nitro-2-naphthol, *o*-nitro-*p*-cresol, dibromo-*o*-nitrophenol, *o*- and *p*-nitrophenolmercurihydroxides, benzoic, cinnamic, *o*- and *m*-nitrobenzoic, 3 : 5-dinitrobenzoic, *o*- and *p*-chlorobenzoic, and *p*-bromobenzoic acids. *p*-Nitrophenol, 2 : 4-dinitrophenol, and 3 : 5-dinitrophenol absorb $1\frac{1}{2}NH_3$. Two molecules of ammonia are absorbed by *p*-bromo-*o*-nitrophenol, 2 : 6-dinitrophenol, 3 : 5-dinitro-*p*-cresol, 5-bromo-3-nitro-*p*-cresol, 4-bromo-2 : 6-dinitrophenol, picric acid, tribromophenol, trichlorophenol, *p*-nitrobenzoic and 2 : 4-dinitrobenzoic acids at the ordinary temperature; by *o*-nitro-*p*-cresol, *o*-nitrophenolmercurihydroxide, and *p*-nitrophenolmercurihydroxide at −10°, and by dibromo-*o*-nitrophenol, *m*- and *p*-nitrobenzoic acids, and *o*-chlorobenzoic acid at −15°. The sodium or potassium salts of the preceding compounds do not absorb ammonia.

Trinitrobenzoic acid absorbs $4NH_3$ at 0°, yielding a black *substance*, which loses $2NH_3$ at 25°. Trinitrobenzene and trinitrotoluene at −10 to −15° absorb $2NH_3$, forming reddish-brown, crystalline *substances.* For these substances, from which the original compounds cannot be regenerated, constitutions such as

$$C_6H_2Me(NO_2)_2\cdot N(NH_2)(ONH_4)\colon O$$

are proposed (compare Hantzsch and Kissel, Abstr., 1900, i, 89).

C. S.

New Method of Formation of Ethers of Glycerol with Phenols. Petar Schivkovitch (*Monatsh.*, 1908, **29**, 951—958).—Brunner obtained a substance, $C_9H_{12}O_4$, during the preparation of quinoldicarboxylic acid by the action of carbon dioxide on quinol in the presence of a hydrogen carbonate and glycerol (Abstr., 1907, i, 319). This substance is probably an ether of glycerol with quinol, but, as it is formed in only very small quantities, it could not be thoroughly investigated. The author has therefore studied the interaction of glycerol with various phenols at 200—210°, and finds that mono-ethers of glycerol are formed.

Phenyl glycerol ether (compare Lindemann, Abstr., 1891, 1198) is formed by heating phenol, glycerol, and sodium acetate together in an atmosphere of hydrogen at 200—210° for twelve to twenty hours. The following derivatives of glycerol are prepared in a similar manner: o-*tolyl ether*, $C_3H_5(OH)_2\cdot O\cdot C_6H_4Me$, glistening needles, m. p. 66°; m-*tolyl ether*, $C_{10}H_{14}O_3$, white needles, m. p. 65°; p-*tolyl ether*, white needles, m. p. 73—74°; *a-naphthyl ether*, $C_{13}H_{14}O_3$, white scales, m. p. 91—92°; *β-naphthyl ether*, $C_{13}H_{14}O_3$, white scales, m. p. 109—110°.

W. H. G.

Preparation of 3-Nitro-2-cyano-1-methoxybenzene, 3-Nitro-2-cyano-1-ethoxybenzene, 4-Nitro-2-cyano-1-methoxybenzene, and 4-Nitro-2-cyano-1-ethoxybenzene. Jan J. Blanksma (*Chem. Weekblad*, 1908, **5**, 789—795).—The preparation of nitrocyano-derivatives of phenetole and anisole is described. 3-Nitro-2-cyano-phenetole (compare Lobry de Bruyn, Abstr., 1885, 656) is prepared from 2 : 3-dinitrophenetole (this vol., i, 157) by the action of alcoholic ammonia, which yields 2-amino-3-nitrophenetole. The amino-group is replaced by the cyano-group by the Sandmeyer reaction. When boiled with acetic anhydride, 3-nitro-2-aminophenetole yields the corresponding acetyl derivative, which crystallises from light petroleum, m. p. 64°. When heated at 120° in alcoholic solution with methylamine, 2 : 3-dinitrophenetole yields 3-*nitro-2-methylaminophenetole*, m. p. 59°, which crystallises from alcohol. Nitric acid, D 1·52, transforms the last compound into 3 : 5-dinitro-2-nitromethylaminophenetole,

$$OEt\cdot C_6H_2\cdot (NO_2)_2\cdot NMe\cdot NO_2,$$

which forms colourless crystals from alcohol, m. p. 79—80° (not 69°, as previously stated, Abstr., 1905, i, 431).

2 : 3-Dinitroanisole was treated analogously to the corresponding dinitrophenetole with alcoholic ammonia, and yielded 3-nitro-*o*-anisidine, $C_6H_3(OMe)(NH_2)(NO_2)$, yellow crystals from alcohol or benzene, m. p. 76° (compare Bantlin, Abstr., 1879, 237). The corresponding acetyl derivative was obtained by the action of acetic anhydride; it has m. p. 128°. The acetylation is much facilitated by addition of a drop of concentrated sulphuric acid to the mixture. The acetylation of

3 : 5-dinitro-*o*-anisidine, $OMe\cdot C_6H_2(NO_2)_2\cdot NH_2$, was similarly effected. The compound formed has m. p. 202°.

Exchange of the NH_2 group for CN by Sandmeyer's method converts 3-nitro-*o*-anisidine into 3-nitro-2-cyanoanisole, colourless leaflets, m. p. 171° (de Bruyn, *loc. cit.*). When heated in alcoholic solution with methylamine at 120°, 2 : 3-dinitroanisole yields 3-nitro-2-methylaminoanisole in the form of dark red needles, readily soluble in alcohol, m. p. 58°. Nitric acid, D 1·52, converts this compound into 3 : 5-dinitro-2-nitrosomethylaminoanisole,

$$MeO\cdot C_6H_2(NO_2)_2\cdot NMe\cdot NO,$$

m. p. 118°.

Reduction of 2 : 4-dinitrophenetole with ammonium sulphide or sodium disulphide yields 4-nitro-*o*-phenetidine, which by Sandmeyer's reaction is converted into 4-*nitro*-2-*cyanophenetole*. It crystallises from boiling water in colourless crystals, m. p. 101°. It is very slightly soluble in cold, but more so in boiling, water, and readily soluble in boiling alcohol. With a mixture of nitric acid and sulphuric acid, it yields 4 : 6-dinitro-2-cyanophenetole, m. p. 72° (Abstr., 1902, i, 281).

4-Nitro-*o*-anisidine yields analogously 4-*nitro*-2-*cyanoanisole*, colourless crystals from boiling water, m. p. 126°, slightly soluble in cold, readily in boiling, alcohol. On treatment with a mixture of nitric acid and sulphuric acid, it is converted into 4 : 6-*dinitro*-2-*cyanoanisole*, which separates from dilute alcohol in colourless crystals, m. p. 71°.

On nitration of 2 : 3-dinitro-anisole (or -phenetole) and 3-nitro-2-cyano-anisole (or -phenetole), the NO_2 group takes up the para-position with reference to the alkyloxy-group; with 4-nitro-2-cyano-anisole (or -phenetole), it takes up the ortho-position. A. J. W.

Nitration of 5-Nitro-1 : 3-dimethoxybenzene. JAN J. BLANKSMA (*Rec. trav. chim.*, 1908, **27**, 251—256).—When 5-nitro-1 : 3-dimethoxybenzene (Vermeulen, Abstr., 1906, i, 256) is treated with nitric acid (D 1·52) in the presence of sulphuric acid, 4 : 5 : 6-*trinitro*-1 : 3-*dimethoxybenzene*, $C_6H(OMe)_2(NO_2)_3$, m. p. 193° (*Rec. trav. chim.*, 1908, **27**, 39), is obtained, together with a small quantity of a compound, m. p. 110°, which has not yet been identified.

The constitution of the trinitro-derivative was determined by converting it by means of alcoholic ammonia into 2 : 6-*dinitro*-3 : 5-*dimethoxyaniline*, $NH_2\cdot C_6H(OMe)_2(NO_2)_2$, m. p. 223°; this yielded 4 : 6-dinitro-1 : 3-dimethoxybenzene, m. p. 155° (Abstr., 1902, i, 715), on diazotisation and subsequent treatment with alcohol (this vol., i, 157), and 4 : 6-dinitroresorcinol, m. p. 210°, was obtained from the latter compound by hydrolysis. The following compounds obtained from 4 : 5 : 6-trinitro-1 : 3-dimethoxybenzene are described :

2 : 6-*Dinitro*-3 : 5-*dimethoxymethylaniline*, $NHMe\cdot C_6H(OMe)_2(NO_2)_2$, m. p. 191°; 2 : 6-*dinitro*-1-*methylnitroamino*-3 : 5-*dimethoxybenzene*, $NO_2\cdot NMe\cdot C_6H(OMe)_2(NO_2)_2$, m. p. 176°, and 2 : 6-*dinitro*-3 : 5-*dimethoxydiphenylamine*, $NHPh\cdot C_6H(OMe)_2(NO_2)_2$, m. p. 190°.

4 : 5-*Dinitro*-1 : 3-*dimethoxybenzene*, m. p. 131°, is obtained when 5-nitro-1 : 3-dimethoxybenzene is treated with nitric acid, D 1·45,

and this is converted into the trinitro-compound described above on further nitration with nitric acid (D 1·52). M. A. W.

Aloesol, a Complex Phenol prepared from Certain Aloes. EUGÈNE LEGÉR (*Compt. rend.*, 1908, **147**, 806—808. Compare this vol., i, 40).—The compound $C_{11}H_4O_3Cl_4$, obtained previously by the author in the chlorination of Cape or Uganda aloes, is not tetrachloromethoxynaphthaquinone, as the author at first supposed, but a derivative of a new phenol, aloesol. *Tetrachloroaloesol* separates from acetic acid in colourless needles, m. p. 268·9° (corr.). This dissolves in alkalis, giving a yellow solution, from which the original compound is precipitated by the addition of excess of alkali. The *acetyl* derivative, $C_{11}H_3O_3Cl_4Ac$, crystallises in pale yellow prisms, m. p. 125° (corr.).

Dichlorotetrahydroaloesol, $C_{11}H_8O_3Cl_2$, prepared by the action of zinc and acetic acid on tetrachloroaloesol, forms colourless, microscopic needles, m. p. 275° (corr.), and in its behaviour towards alkalis resembles tetrachloroaloesol. The *barium* compound, $(C_{11}H_7O_3Cl_2)_2Ba$, forms long, colourless needles. The *acetyl* derivative occurs in colourless, prismatic needles, m. p. 150—151° (corr.). A yellow modification, however, is formed when acetic anhydride is employed, and this furnishes, on hydrolysis, a yellow modification of dichlorotetrahydroaloesol having the same m. p. as the colourless variety.

The presence of a benzene ring in tetrachloroaloesol is indicated by the fact that nitric acid decomposes it with formation of oxalic acid and tetrachloroquinone. W. O. W.

Preparation of a Compound having the Composition of Nitrosobenzyl Alcohol. KALLE & Co. (D.R.-P. 199317).—The monomercury derivative of *o*-nitrotoluene (compare Abstr., 1907, i, 908) when treated with cold concentrated hydrochloric acid gives rise to an unstable compound, isolated by extraction with ether or distillation in steam, and having the composition of an *o*-nitrosobenzyl alcohol, $NO\cdot C_6H_4\cdot CH_2\cdot OH$; this product gives with mercuric chloride an additive compound crystallising from benzene in white needles. When 6% hydrochloric acid is employed in this reaction, the anhydride, anthranil, is obtained. G. T. M.

***o*-, *m*-, and *p*-Tolylethyl Alcohols.** K. KLING (*Bull. Acad. Sci. Cracow*, 1908, 632—633).—By the energetic electrolytic reduction of *o*-, *m*-, and *p*-tolylacetic acids, the corresponding alcohols have been obtained. o-*Tolylethyl alcohol*, $C_7H_7\cdot CH_2\cdot CH_2\cdot OH$, has b. p. 243—243·5° (corr.), D_4^{20} 1·0159, and n_D 1·5214. The *meta*-isomeride has b. p. 242·5—243° (corr.), D_4^{20} 1·0127, and n_D 1·5231, and the *para*-compound has b. p. 244·5—245° (corr.), D_4^{20} 1·0177, and n_D 1·5271. C. S.

Isolation of Cholesterol from Fats. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1908, **57**, 515—519).—Glikin adversely criticises a method he incorrectly attributes to the author. References are given to an improved method, published in the author's Festschrift, and a brief account of it is again published. W. D. H.

Allylhippuric Acid. A Convenient Material for the Preparation of γδ-Disubstituted α-Amino-*n*-valeric Acids. Sören P. L. Sörensen (*Ber.*, 1908, 41, 3387—3390. Compare Abstr., 1905, i, 749; also Fischer and Krāmer, this vol., i, 858).—When ethyl allylphthaliminomalonate is hydrolysed with sodium hydroxide and then evaporated with hydrochloric acid, allylglycine is formed, and this, when benzoylated, yields r-*allylhippuric acid*,

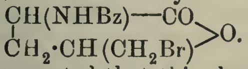
$$CH_2{:}CH\cdot CH_2\cdot CH(NHBz)\cdot CO_2H,$$

which crystallises from benzene in rectangular plates, m. p. 107—107·5°. The racemic acid can be resolved by means of brucine or quinidine; with the former base, the salt of the *l*-acid crystallises first, and with the latter base, the salt of the *d*-acid.

The active acids combine with bromine, yielding γδ-dibromo-α-benzoylaminovaleric acid,

$$CH_2Br\cdot CHBr\cdot CH_2\cdot CH(NHBz)\cdot CO_2H,$$

as an oil, and this readily loses hydrogen bromide, forming a crystalline lactone,



$$\begin{array}{l} CH(NHBz)—CO \\ | \\ CH_2\cdot CH(CH_2Br) \end{array}\!\!>O.$$

It is suggested that this should be used for the syntheses of α-amino-γδ-dihydroxy- and other γδ-substituted valeric acids. J. J. S.

***o*-Bromophenyl- and α-Bromophenyl-acetamides.** Wilhelm Steinkopf and Czeslau Benedek (*Ber.*, 1908, 41, 3595—3598).—Attempts to prepare nitrated phenylacetamides for the purpose of comparison with nitroacetamide have been unsuccessful. In the course of the work, the authors have prepared two brominated phenylacetamides. These are now described.

o-*Bromophenylacetamide*, $C_6H_4Br\cdot CH_2\cdot CO\cdot NH_2$, prepared by the action of bromine on phenylacetamide suspended in water, separates in white crystals, m. p. 181°, and on treatment with sodium nitrite in sulphuric acid solution yields *o*-bromophenylacetic acid.

α-Bromophenylacetamide, $CHBrPh\cdot CO\cdot NH_2$, prepared by treating α-bromophenylacetyl chloride in benzene solution with a current of dry ammonia, forms white crystals, m. p. 143—144°, and on hydrolysis with nitrous acid yields α-bromophenylacetic acid, m. p. 87°.

G. Y.

Halogen Amino-acids: *p*-Iodophenylalanine. Henry L. Wheeler and Samuel H. Clapp (*Amer. Chem. J.*, 1908, 40, 458—468. Compare this vol., i, 897).—In continuation of their work, the authors have synthesised *p*-iodophenylalanine.

Ethyl phthalimino-p-*iodobenzylmalonate*,

$$C_6H_4{:}(CO)_2{:}N\cdot C(CO_2Et)_2\cdot CH_2\cdot C_6H_4I,$$

prepared by heating *p*-iodobenzyl bromide with ethyl sodiophthaliminomalonate, forms flat, colourless prisms or six-sided plates, m. p. 112°. On alkaline hydrolysis and subsequent acidification, it gives *phthalamic*-p-*iodobenzylacetic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4I,$$

in needles, m. p. 179°; if, on acidification with hydrochloric acid, the precipitate is digested with the acid for two hours, p-*iodophenylalanine*, $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot C_6H_4I$, is produced, forming thin scales,

m. p. 270° (decomp.). The *hydrochloride*, thin, flat, colourless plates, decomposing at 248°, and *silver* and *copper* salts are described. The *phenylcarbimide* forms aggregates of flat prisms or plates, m. p. 178—179° (decomp.). The *hydantoin*, $C_{16}H_{13}O_2N_2I$, prepared from this by boiling with 20% hydrochloric acid, forms flat, rhombohedral crystals, m. p. 195—196°. The *ethyl* ester of *p*-iodophenylalanine is a colourless, viscid oil, b. p. 223—226°/25 mm., of which the *picrate* forms flat, yellow plates or tablets, m. p. 200—203°. J. C. C.

p-Dimethylaminocinnamic Acid. Lotte Weil (*Monatsh.*, 1908, 29, 895—908).—The object of this investigation was to ascertain if a methylamino- or dimethylamino-group influences the replacement of α-halogen atoms by methoxy- or ethoxy-groups in the same manner as alkyloxy-groups (compare Hertzka, Abstr., 1905, i, 291; Werner, Abstr., 1906, i, 180; Goldschmiedt, Abstr., 1907, i, 241). β-Bromo-*p*-dimethylaminocinnamic acid was therefore prepared, and was found to be quite stable towards boiling alcohol and aqueous potassium hydroxide, so that a *p*-dimethylamino-group does not exert the same influence on an α-halogen atom as a *p*-methoxy-group. The *p*-dimethylamino-group was found, however, to have a great influence on the alkylcarboxy-group, for methyl *p*-dimethylaminocinnamate cannot, like methyl cinnamate, be converted by ammonia into the corresponding amide.

p-*Dimethylaminocinnamic acid*, $NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$, may be prepared by Perkin's method provided potassium acetate is used in the place of the sodium salt; it crystallises in glistening, yellow leaflets, m. p. 216° (decomp.); the *silver* salt is yellow. The *ethyl* ester, $C_{13}H_{17}O_2N$, is most readily obtained by the action of sodium on a mixture of ethyl acetate and *p*-dimethylaminobenzaldehyde; it crystallises in golden-yellow leaflets, m. p. 74—75°, b. p. 205—208°/19 mm.; the *picrate*, $C_{13}H_{17}O_2N,C_6H_3O_7N_3$, forms red crystals, m. p. 130—132°. The *methyl* ester, $C_{12}H_{15}O_2N$, forms pale yellow crystals, m. p. 134—136°; it is converted by bromine in chloroform into a bromo-derivative, which forms colourless crystals, m. p. 164—168° (decomp.), and is either *methyl αβ-dibromo-*p*-dimethylamino-β-phenylpropionate*, $NMe_2\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot CO_2Me$, or *methyl β-bromo-*p*-dimethylaminocinnamate hydrobromide*, $NMe_2\cdot C_6H_4\cdot CBr{:}CH\cdot CO_2Me,HBr$. The substance just described is converted by boiling water, alcohol, or aqueous potassium hydroxide into *methyl β-bromo-*p*-dimethylaminocinnamate*, $NMe_2\cdot C_6H_4\cdot CBr{:}CH\cdot CO_2Me$, an exceedingly stable compound crystallising in glistening, yellow leaflets, m. p. 96°; it is not affected by aqueous potassium hydroxide, but is converted by alcoholic potassium hydroxide into *β-bromo-*p*-dimethylaminocinnamic acid*, $C_{11}H_{12}O_2NBr$, yellow crystals, m. p. 165°, and p-*dimethylaminoacetophenone*,

$$NMe_2\cdot C_6H_4\cdot COMe,$$

crystallising in long needles, m. p. 103°. The latter compound may also be obtained by treating *p*-aminoacetophenone with methyl sulphate; the *phenylhydrazone* forms pale yellow crystals, m. p. about 150°. The substance, m. p. 59°, described by Klingel (Abstr., 1886, 61) is not *p*-dimethylaminoacetophenone, as stated by this author.

p-*Dimethylamino-β-phenylpropionic acid*, $NMe_2\cdot C_6H_4\cdot C_2H_4\cdot CO_2H$, is obtained as its sodium salt by treating ethyl *p*-dimethylaminocinnamate in alcohol with sodium; it crystallises in colourless leaflets, m. p. 104°.

p-*Dimethylaminobenzaldehyde*-p-*bromophenylhydrazone*, $C_{15}H_{16}N_3Br$, crystallises in brown, felted needles, m. p. 181°.

p-*Aminoacetophenonephenylhydrazone* has m. p. 112°. W. H. G.

Action of Nascent Hypoiodous Acid on Unsaturated Acids. J. Bougault (*Ann. Chim. Phys.*, 1908, [viii], 15, 296—312).—A detailed account of work already published (compare this vol., i, 179, 269, 340, 791). The action of iodine in the presence of sodium carbonate or hydrogen carbonate on certain $\beta\gamma$-unsaturated acids is quantitative, and can be employed for the volumetric estimation of hydropiperic and phenyl*iso*crotonic acids. M. A. W.

Preparation of Arylthioglycollic [Arylthiolacetic] Acids. Kalle & Co. (D.R.-P. 201231 and 201232. Compare this vol., i, 672).—The condensation of a diazonium salt with a thioglycollic acid occurs more readily and at lower temperatures (20—25°) in the presence of "molecular copper." A good yield of *o*-carboxyphenylthiolacetic acid is obtained by condensing diazotised anthranilic acid with thioglycollic acid in warm alkaline solution; the intermediate product is precipitated by acids, dissolved in aqueous sodium carbonate, and the solution heated to boiling until all the nitrogen is expelled, when the final product is obtained by cooling and acidifying. G. T. M.

Some Oximes of the o-Nitrotoluene Series and their Changes. Arnold Reissert (*Ber.*, 1908, 41, 3810—3816).—On boiling with water, the oxime of *o*-nitrophenylglyoxylic acid yields *o*-nitrobenzonitrile and carbon dioxide, and this oxime was supposed to be formed as an intermediate product in the conversion of *o*-nitrophenylpyruvic acid oxime by nitrous acid into the *o*-nitrobenzonitrile (Abstr., 1897, i, 417). Further inquiry has, however, shown that by slowly adding a sodium nitrite solution at the bottom of a dilute hydrochloric acid solution of the *o*-nitrophenylpyruvic acid at 60° and afterwards heating to 100°, a 90% yield of *o*-nitrobenzonitrile and oxalic acid is obtained. The oxalic acid can only be produced by the decomposition of the oximino-*o*-nitrobenzoylglyoxylic acid, thus:

$$NO_2\cdot C_6H_4\cdot C(:NOH)\cdot CO\cdot CO_2H = NO_2\cdot C_6H_4\cdot CN + C_2O_4H_2,$$

and the assumption of the intermediate formation of the nitrophenylglyoxylic acid is incorrect.

Oximino-o-nitrophenylpyruvic acid,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot C(:NOH)\cdot CO_2H,$$

obtained from the acid and hydroxylamine, crystallises in almost colourless needles, m. p. 161° (decomp.), and is hydrolysed by mineral acids into its components. When boiled with water, it is slowly converted into *o*-nitrophenylacetonitrile. A small quantity of o-*nitrophenylacetamide*, $C_8H_8O_3N_2$, colourless crystals, m. p. 160—161°, was also isolated; it was also obtained by heating ethyl *o*-nitrophenylacetate with alcoholic ammonia under pressure at 100°. The nitrophenylacetonitrile is formed by heating the oxime of nitrophenylpyruvic acid at 140—145°.

The liability of these oximes to change into nitriles depends on the presence of negative contiguous groups, CO_2H and $\cdot CO\cdot CO_2H$, as *o*-nitrobenzaldoxime is more stable. The conversion of this oxime into *o*-nitrobenzonitrile or its amide is accomplished if small quantities of alkaline substances, like borax, potassium cyanide, or sodium carbonate, are added to the water and the mixture heated for some hours. W. R.

Preparation of *o*-Carboxyphenylthioglycollic [α-Carboxyphenylthiolacetic] Acid. KALLE & Co. (D.R.-P. 199249).—*o-Carboxyphenylthiolacetic acid*, $CO_2H\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$, yellow crystals, m. p. 213°, was obtained by the interaction of the sodium salts of *o*-thiolbenzoic and chloroacetic acids in aqueous solution; it finds employment in the production of dyes and pharmaceutical products. G. T. M.

Preparation of the Anhydrides of Acylsalicylic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 201325 and 201326).—The therapeutic employment of the acylsalicylic acids is attended with two disadvantages—their distinctly acid taste and their appreciably irritating action on the sensitive mucous lining of the stomach. Their anhydrides, which have now been prepared, are free from these disagreeable properties.

Acetylsalicylic [*o-acetoxybenzoic*] *anhydride*, $O(CO\cdot C_6H_4\cdot OAc)_2$, white crystals, m. p. 85°, is obtained by condensing acetylsalicylic acid in benzene solution with thionyl chloride, carbonyl chloride, trichloromethyl formate, or hexachlorodimethyl carbonate in the presence of pyridine.

Acetylsalicylyl [*o-acetoxybenzoyl*] *chloride*, colourless crystals, m. p. 43—44°, b. p. 135°/12 mm., from phosphorus pentachloride and acetylsalicylic acid, when warmed with this acid (1 mol.) and dimethylaniline in toluene solution, or when heated with sodium acetylsalicylate, also gives rise to the same anhydride.

The *ethyl carbonate* compound, $O(CO\cdot C_6H_4\cdot O\cdot CO_2Et)_2$, clusters of needles, m. p. 74°, was obtained from the corresponding acid by the action of sulphuryl chloride and pyridine in benzene solution. *Benzoylsalicylic anhydride*, m. p. 106—107°, was prepared from the corresponding acid by means of carbonyl chloride and quinoline in benzene solution, and *cinnamoylsalicylic anhydride*,

$$O(CO\cdot C_6H_4\cdot O\cdot CO\cdot CH{:}CHPh)_2,$$

m. p. 114—116°, was obtained from cinnamoylsalicylic acid (Proc., 1906, **22**, 317) by the action of carbonyl chloride and antipyrine in benzene solution.

Other condensing agents, such as acetyl chloride, phosphoryl chloride, and phosphorus tribromide and trichloride, may be employed in the production of these anhydrides. G. T. M.

Rule in Benzoylation of Aromatic Hydroxy-acids and their Esters. LASSAR-COHN and JOSEF LÖWENSTEIN (*Ber.*, 1908, **41**, 3360—3367).—It has been found that the hydroxyl cannot be benzoylated in a hydroxy-compound containing a carboxyl or a sulphonic group in any position in the ring by the Schotten-Baumann method, but that its esters give benzoates. The following benzoates have been prepared.

Benzoylsalicylic [o-*benzoyloxybenzoic*] *acid*, $C_{14}H_{10}O_4$, obtained in small yield by stirring together dipotassium salicylate and benzoyl chloride in light petroleum, crystallises from dilute alcohol; m. p. 132°. It is easily hydrolysed by alkali. The greater portion of the product of the reaction is insoluble in water, and when distilled gives benzoic acid and its phenyl ester. Methyl benzoylsalicylate (benzosalin: D.R.-P. 169247) is obtained in quantitative yield by the Schotten-Baumann method; m. p. 92°, b. p. 350—358° (decomp.), 270—280°/120 mm. *Ethyl* p-*benzoyloxybenzoate*, $C_{16}H_{14}O_4$, has m. p. 94°, b. p. 358—360°; the ester of *m*-hydroxybenzoic acid is hydrolysed under the conditions of the experiment, and no benzoyl derivative was obtained.

Ethyl β-benzoyloxynaphthoate, $C_{20}H_{16}O_4$, has m. p. 98° and b. p. 342—345°. The α-hydroxy-β-naphthoic acid (Abstr., 1888, 60) is considered to be the 2-hydroxynaphthalene-1-carboxylic acid because it is not esterified by hydrogen chloride and alcohol. The *ethyl* ester, $C_{13}H_{12}O_3$, has m. p. 46°, and gives the *benzoate*, $C_{20}H_{16}O_4$, m. p. 51°.

Crude ethyl phenol-*p*-sulphonate, obtained by the action of ethyl iodide on the silver salt, gives the *benzoate*, $C_{15}H_{14}O_5S$, m. p. 62°. W. R.

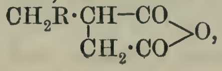
Simultaneous Formation of Isomeric Substitution Products of Benzene. ARNOLD F. HOLLEMAN. **XI. Nitration of Phthalic and *iso*Phthalic Acids.** J. HUISINGA (*Rec. trav. chim.*, 1908, 27, 260—286).—A detailed account of work already published (Abstr., 1907, i, 136). The percentage solubilities of 3-nitrophthalic, anhydrous 5-nitro*iso*phthalic, hydrated 5-nitro*iso*phthalic, 4-nitro*iso*phthalic, and 2-nitro*iso*phthalic acids at 25° are 2·048, 0·220, 0·157, 0·967, and 0·216 respectively. M. A. W.

Colour Reactions during the Hydrolysis of Acid Anhydrides. HANS STOBBE (*Ber.*, 1908, 41, 3720—3725).—In the hydrolysis of certain colourless anhydrides to the colourless salts of the corresponding dibasic acids by means of alkali hydroxides, the author has noticed the appearance of an evanescent coloration. The actual colour depends on the particular anhydride, and may be yellow, red, violet, or blue. It is shown that the production of a coloration is characteristic of anhydrides containing either of the following groupings:

$$C_6H_5\cdot C\colon C\cdot CO\cdot O\cdot \text{ or } C_6H_4\colon C\colon C\cdot CO\cdot O\cdot.$$

Examples of compounds which give such colorations are phenylitaconic anhydride, the two stereoisomeric phenylmethylitaconic anhydrides, diphenylitaconic anhydride, γ-diphenyleneitaconic anhydride, and the anhydrides of 1-phenyl-1 : 2-dihydronaphthalene-2 : 3-dicarboxylic acid and the corresponding 1 : 4-diphenyl-2 : 3-dicarboxylic acid.

Dimethylitaconic anhydride, the reduced itaconic anhydrides,



$$\begin{array}{l}CH_2R\cdot CH-CO \\ \quad\;\;\; | \\ \quad\;\; CH_2\cdot CO\end{array}\!\!>O,$$

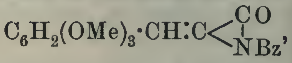
and the anhydrides of tetrahydronaphthalenedicarboxylic acids do not give colorations.

Experiments have been made by mixing together absolute alcoholic sodium hydroxide with solutions of the anhydrides in various solvents, and determining the time during which the coloration persisted. It was found that in the presence of acetone the colour was retained for a much longer time, especially when the volume of acetone used was relatively large. In all experiments, 1 c.c. of *N*/10 sodium hydroxide and 0·0003 gram of anhydride were used.

In the case of the two stereoisomeric phenylmethylitaconic anhydrides, the colorations were so fugitive that even with acetone the solutions became quite colourless after a few seconds.

Alcohols have a similar effect to ketones, but benzene, chloroform, and carbon tetrachloride have little effect. Alcoholic solutions of other bases have also been used. J. J. S.

Synthesis of Trimethylhomogallic Acid (Methyliridic Acid). Ferdinand Mauthner (*Ber.*, 1908, 41, 3662—3665).—3 : 4 : 5-Trimethoxybenzaldehyde (this vol., i, 348), hippuric acid, anhydrous sodium acetate, and acetic anhydride, when heated on the water-bath for one and a-half hours, yield the *substance*,



$C_6H_2(OMe)_3\cdot CH{:}C{<}\begin{array}{l}CO\\ \,|\\ NBz\end{array}$,

m. p. 165—166°. which is hydrolysed by dilute sodium hydroxide, ammonia, benzoic acid, and 3 : 4 : 5-*trimethoxyphenylpyruvic acid*, $C_6H_2(OMe)_3\cdot CH_2\cdot CO\cdot CO_2H$, m. p. 167—168°, being formed. The last-mentioned acid forms an *oxime*, $C_{12}H_{15}O_6N$, m. p. 155—156°, and with *o*-phenylenediamine hydrochloride, yields a *trimethoxybenzylquinoxalone*, $C_{18}H_{18}O_4N_2$, m. p. 196—197°, and is converted by hydrogen peroxide in alkaline solution into trimethylhomogallic [3 : 4 : 5-trimethoxyphenylacetic] acid, $C_6H_2(OMe)_3\cdot CH_2\cdot CO_2H$. C. S.

[Preparation of Triphenylmethane Colouring Matters from Diortho-substituted Benzaldehydes]. Anilinfarben- & Extract-Fabriken vormals. J. R. Geigy in Basel (D.R.-P. 199943).—The diortho-substituted benzaldehydes, when condensed with *o*-cresotic acid, give rise to triphenylmethane colouring matters, which have valuable tinctorial properties, being faster to light and alkalis, and dyeing wool in acid-bath in deeper shades, than those from the mono-ortho-substituted benzaldehydes. The following new aldehydes are described :

2 : 6-*Dichlorobenzaldehyde*, colourless needles, m. p. 70—71° ; 2 : 6-*dichloro*-3-*nitrobenzaldehyde*, colourless leaflets, m. p. 76—77° ; 2 : 6-*dichlorobenzaldehyde*-3-*sulphonic acid* ; 2-*chlorobenzaldehyde*-6-*sulphonic acid* ; *benzaldehyde*-2 : 6-*disulphonic acid*, and 6-*chlorobenzaldehyde*-2 : 4-*disulphonic acid* ; the sodium salts of all these acids, excepting the last, are salted out in colourless needles ; 2 : 3 : 6- and 2 : 4 : 6-*trichlorobenzaldehydes* form colourless needles, melting at 86—87° and 58—59° respectively. G. T. M.

Condensation of *cyclo*Pentanone with Benzaldehyde. Max Kauffmann (*Ber.*, 1908, 41, 3726—3727).—In the preparation of dibenzylidene*cyclo*pentanone (Vörlander and Hobohm, Abstr., 1896, i, 603), it is necessary that the alkali hydroxide solution used should not be too dilute. The author finds that very dilute alkali solutions, or solutions of weak alkalis, such as ammonia, trimethylamine, or sodium carbonate, bring about condensations, but that the products formed are quite different from the sparingly soluble dibenzylidene*cyclo*pentanone. Some of these products are oily, others have comparatively low m. p.'s ; some are colourless, whereas others are yellow. J. J. S.

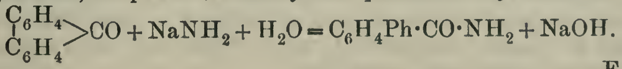
Preparation of Colouring Matters of the Thioindigo-Red Series. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 198509).—*Bis-o-thioacetophenone*, $S_2(C_6H_4\cdot COMe)_2$, a substance analogous to indigo-red, is produced by passing air through a solution of *o*-thiolacetophenone in aqueous sodium hydroxide. Other oxidising agents, such as alkali ferricyanides, persulphates, perborates, or percarbonates, may be employed. This red colouring matter is also obtained by heating *o*-thiolacetophenone with crystallised sodium sulphide ; this operation gives rise to the leuco-derivative, which is oxidised as before by aerial oxidation in alkaline solution.

G. T. M.

Products of the Action of Sodamide on Ketones. Albin Haller and Ed. Bauer (*Compt. rend.*, 1908, 147, 824—826. Compare Abstr., 1906, i, 441).—When a benzene or toluene solution of benzophenone is heated to boiling with sodamide, in some cases an abundant white precipitate is formed, with or without the previous production of an intense blue coloration, whilst in other cases the sodamide slowly dissolves with or without the subsequent separation of a deposit. The production of the blue colour is probably due to the action of free sodium contained in the sodamide (compare Schorigin, this vol., i, 866). The more nearly anhydrous the solution the slower the precipitate is in forming. By collecting the precipitate, drying, and treating with water, benzamide, mixed with a little benzoic acid, is formed. When decomposed with dilute ammonia, benzamide only is formed. The reactions can be represented thus : $COPh_2 + NaNH_2 = NH_2\cdot CPh_2\cdot ONa$; $NH_2\cdot CPh_2\cdot ONa + H_2O = NH_2\cdot COPh + C_6H_6 + NaHO$. If freshly-prepared sodamide free from sodium is used, and the solvent is absolutely anhydrous, no deposit is formed in the hot solution, but the substance separates after a time as an abundant crystalline crust of the composition $NH_2\cdot CPh_2\cdot ONa$, which, when treated with water, regenerates the whole of the benzophenone, and gives theoretical quantities of sodium hydroxide and ammonia, thus :

$$NH_2\cdot CPh_2\cdot ONa + H_2O = COPh_2 + NaOH + NH_3.$$

Under the same conditions, phenyl *p*-tolyl ketone gives an almost equimolecular mixture of benzamide and toluoylamide, whilst phenyl anisyl ketone yields rather more anisamide than benzamide. Fluorenone, when treated in toluene solution with sodamide, gives diphenyl-*o*-carboxylamide, m. p. 177°, directly and quantitatively, thus :



$$\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>CO + NaNH_2 + H_2O = C_6H_4Ph\cdot CO\cdot NH_2 + NaOH.$$

E. H.

Action of Alcoholic Potassium Hydroxide Solution on Ketones. P. J. MONTAGNE (*Rev. trav. chim.*, 1908, **27**, 327—359. Compare Abstr., 1907, i, 854).—Zagumenny (Abstr., 1877, 459) has shown that benzhydrol is produced when benzophenone is heated at 160° with alcoholic potassium hydroxide. The author finds the same reduction occurs when the ketone is boiled for two days with a 20% alcoholic solution of potassium hydroxide, and that substituted derivatives of benzophenone, when similarly treated, are either reduced similarly or are decomposed, yielding benzoic acid and the substituted benzene. Thus 4-chloro-, 4-bromo-, 4-methyl-, or 4-phenyl-benzophenone yields the corresponding substituted benzhydrol, whilst 2 : 4 : 6-trichlorobenzophenone yields trichlorobenzene and benzoic acid ; 2 : 4 : 6-tribromobenzophenone yields 4-bromobenzhydrol ; 2 : 4 : 6-trimethylbenzophenone remains unaltered, and phenyl α-naphthyl ketone yields phenyl-α-naphthylcarbinol.

The following new compound was prepared in the course of the work : 2 : 4 : 6-*tribromobenzophenone*, $C_6H_2Br_3{\cdot}COPh$, obtained by heating benzoyl chloride, 1 : 3 : 5-tribromobenzene, and aluminium chloride at 150—160°, forms colourless, shining, triclinic crystals [F. M. JAEGER, $a : b : c = 1{\cdot}3939 : 1 : 1{\cdot}1065$; $\alpha = 130°\ 36'$, $\beta = 122°\ 59'$, $\gamma = 58°\ 58'$], D^{15} 2·034, m. p. 147°, b. p. 405°/765 mm. The same compound was also prepared from 2 : 4 : 6-tribromobenzoyl chloride (Sudborough, Trans., 1895, **67**, 596) and benzene in the presence of aluminium chloride. The crystallographic measurements by F. M. Jaeger of the following compounds are recorded : 2-bromobenzophenone forms large, colourless, monoclinic prisms [$a : b : c = 0{\cdot}5045 : 1 : 0{\cdot}9322$; $\beta = 83°\ 24{\cdot}5'$], D^{14} 1·517 ; phenylindoxazen forms colourless, rhombic crystals [$a : b : c = 0{\cdot}7905 : 1 : 1{\cdot}2600$], D^{15} 1·295 ; 2 : 4 : 6-tribromobenzonitrile crystallises in the monoclinic system [$a : b : c = 1{\cdot}2113 : 1 : 1{\cdot}1025$; $\beta = 44°\ 23{\cdot}75'$] ; 2 : 4 : 6-tribromobenzamide crystallises from alcohol in long needles, which, in contact with the mother liquor, change into monoclinic prisms [$a : b : c = 2{\cdot}1655 : 1 : 1{\cdot}1092$; $\beta = 83°\ 45'$] ; 2 : 4 : 6-tribromobenzoyl chloride forms colourless, triclinic prisms [$a : b : c = 1{\cdot}9341 : 1 : 1{\cdot}0041$; $\alpha = 89°\ 54{\cdot}6'$, $\beta = 108°\ 43{\cdot}75'$, $\gamma = 84°\ 21'$]. M. A. W.

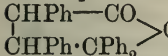
Reactions of Organic Magnesium Compounds with Cinnamylidene Esters. II. Reactions with Methyl α-Phenylcinnamylideneacetate. MARIE REIMER and GRACE POTTER REYNOLDS (*Amer. Chem. J.*, 1908, **40**, 428—444. Compare Abstr., 1907, i, 852). —It was shown previously that the compounds produced by the action of organic magnesium compounds on methyl cinnamylidenemalonate are formed by 1 : 4-addition, and the authors have now extended the reaction to the case of methyl α-phenylcinnamylideneacetate. The reaction proceeds with much greater difficulty than in the previous cases examined, and the resulting compounds are not esters, formed by 1 : 4-addition, but ketones or tertiary alcohols, formed by replacement of the methoxyl group and subsequent addition of a second molecule of reagent in the 1 : 4- or 1 : 2-position, according to the nature of the magnesium compound.

αβ-Diphenyl-γ-benzylidenebutyrophenone,

$$\mathrm{CHPh{:}CH{\cdot}CHPh{\cdot}CHPh{\cdot}COPh},$$

prepared by the action of magnesium phenyl bromide (3 mols.) on methyl α-phenylcinnamylideneacetate (1 mol.) in boiling ethereal solution, crystallises in slender, soft, white needles, m. p. 191·5—192·5°. When oxidised with permanganate, it yields *β-benzoyl-αβ-diphenylpropionic acid*, $\mathrm{CHPhBz{\cdot}CHPh{\cdot}CO_2H}$, which crystallises with 1EtOH in small, shining needles, m. p. 211—212°; the *methyl* ester forms shining, white needles, m. p. 159°.

αβ-Diphenyl-γ-benzylidenebutyrophenone reacts with magnesium phenyl bromide, yielding a tertiary alcohol which could not be isolated in the pure state; on oxidation, it gives *αβγγ-tetraphenylbutyrolactone*,



$\left.\begin{array}{l}\mathrm{CHPh{-}CO}\\ \mathrm{CHPh{\cdot}CPh_2}\end{array}\right>\mathrm{O}$, crystallising in slender needles, m. p. 221—221·5°, and, on distillation under diminished pressure, it yields a yellow oil, from which separates a *compound*, $\mathrm{C_{22}H_{18}O}$, probably phenylbenzylidenepropiophenone, crystallising in needles, m. p. 134—135°.

Bromo-αβ-diphenyl-γ-benzylidenebutyrophenone,

$$\mathrm{CPhBr{:}CH{\cdot}CHPh{\cdot}CHPh{\cdot}COPh},$$

or, less probably, $\mathrm{CHPh{:}CBr{\cdot}CHPh{\cdot}CHPh{\cdot}COPh}$, forms white needles, m. p. 186—187°.

Benzyl α-phenyl-β-benzyl-γ-benzylidenepropyl ketone,

$$\mathrm{CHPh{:}CH{\cdot}CH(CH_2Ph){\cdot}CHPh{\cdot}CO{\cdot}CH_2Ph},$$

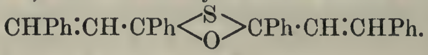
prepared by the interaction of magnesium benzyl bromide and methyl α-phenylcinnamylideneacetate, forms slender, white needles, m. p. 150°. Magnesium *o*-tolyl or naphthyl bromides do not react with the ester, but magnesium methyl iodide in excess furnishes an oil (probably containing the tertiary alcohol,

$$\mathrm{CHPh{:}CH{\cdot}CH{:}CPh{\cdot}CMe_2{\cdot}OH}),$$

which, on distillation under reduced pressure, loses water and yields a *hydrocarbon*, $\mathrm{CHPh{:}CH{\cdot}CH{:}CPh{\cdot}CMe{:}CH_2}$, white crystals, m. p. 97—98°, b. p. 140—150°/25 mm. J. C. C.

Thio-derivatives of Ketones. VI. Emil Fromm (*Ber.*, 1908, 41, 3644—3661).—Whilst two isomeric forms of trithioaldehydes are known in accordance with stereochemical views, attempts to obtain stereoisomerides of trithioketones, derived from ketones of the type $\mathrm{R{\cdot}CO{\cdot}R'}$, have hitherto been unsuccessful (compare Fromm and Baumann, Abstr., 1895, i, 362; Fromm and Ziersch, Abstr., 1906, i, 930; Fromm and Höller, Abstr., 1907, i, 710).

[With W. Lambrecht.]—The authors have now succeeded in obtaining two stereoisomeric, half-sulphurised thioketones by the action of ammonia and hydrogen sulphide on an alcoholic solution of benzylideneacetophenone. The one or the other isomeride is obtained according as the ammonia or the hydrogen sulphide is introduced first into the alcoholic solution. If the solution is saturated with hydrogen sulphide, cooled to 0°, treated with a large excess of ammonia, and left overnight, a quantitative yield of *β-duplobenzylideneacetophenone sulphide* [*monothioduplobenzylideneacetophenone*], $\mathrm{C_{30}H_{24}OS}$, m. p. 181°, is obtained as an amorphous, white powder. The *α-isomeride*, m. p. 96°, is obtained when an alcoholic solution of benzylideneacetophenone is saturated with ammonia, cooled, and treated with hydrogen sulphide. The two substances show the same reactions. For example, dry distillation causes the formation of benzylideneacetophenone and unexamined products containing sulphur; reduction by zinc dust and glacial acetic acid yields benzylacetophenone, whilst the action of phenylhydrazine in boiling glacial acetic acid results in the formation of hydrogen sulphide and triphenylpyrazoline. These reactions, which show that the skeleton of benzylideneacetophenone is still existent in the two isomerides, are in harmony with the formula

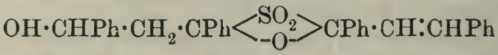


$$\mathrm{CHPh{:}CH{\cdot}CPh}<\substack{\mathrm{S}\\ \mathrm{O}}>\mathrm{CPh{\cdot}CH{:}CHPh.}$$

It is a matter of doubt whether the stereoisomerism is connected with the ethylenic linkings or is conditioned by the disposition of the groups about the plane of the heterocyclic ring. Since, however, the more fusible α-duplobenzylideneacetophenone sulphide is transformed into the β-isomeride by the rapid evaporation of its solution in chloroform containing iodine, the latter view is the more favoured, the α-isomeride having the *cis*-configuration.

If a chloroform solution of either isomeride is treated with bromine in chloroform, and alcohol is then added, sulphur is eliminated, the solution becomes decolorised, and Rupe and Schneider's β-bromo-ω-benzylacetophenone (Abstr., 1895, i, 361) is precipitated. In the absence of the alcohol, decolorisation occurs more slowly, hydrogen bromide is evolved, and a *tribromide*, $C_{30}H_{25}OBr_3S$, m. p. 147°, is obtained. The α- or the β-isomeride with excess of iodine in chloroform yields a *substance*, $C_{30}H_{28}O_3S$, m. p. 191°.

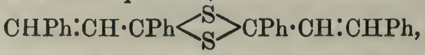
When chloroform solutions of the α- and β-isomerides are oxidised by potassium permanganate and dilute sulphuric acid, stereoisomeric oxidation products are obtained. This result is noteworthy, since stereoisomeric trithioaldehydes yield the same oxidation product. The *substance*, $C_{30}H_{26}O_4S$, m. p. 216°, obtained by the oxidation of β-duplobenzylideneacetophenone sulphide, forms small, white prisms, whilst the oxidation product of the α-isomeride, m. p. 198°, crystallises in needles and is transformed by iodine into its isomeride. Little has been settled regarding the constitution of these oxidation products; they are stable to phenylhydrazine, or benzoyl chloride and sodium hydroxide, or hydrogen chloride in cold glacial acetic acid. They yield benzylideneacetophenone by treatment with hot acetic anhydride and sodium acetate. The formula



$$\mathrm{OH{\cdot}CHPh{\cdot}CH_2{\cdot}CPh}<\substack{\mathrm{SO_2}\\ \mathrm{-O-}}>\mathrm{CPh{\cdot}CH{:}CHPh}$$

is proposed, but is contrary to the fact that the oxidation products cannot be acetylated or benzoylated.

Duplobenzylidenethioacetophenone,



$$\mathrm{CHPh{:}CH{\cdot}CPh}<\substack{\mathrm{S}\\ \mathrm{S}}>\mathrm{CPh{\cdot}CH{:}CHPh,}$$

m. p. 191°, is obtained in a bad yield when hydrogen chloride, followed by an excess of hydrogen sulphide, is led into an alcoholic solution of benzylideneacetophenone at 0°; it is decomposed by phenylhydrazine, yielding hydrogen sulphide and a substance which is probably triphenylpyrazoline.

[With JAMES L. McKEE.]—With the hope of preparing another compound possessing the peculiar additive properties of duplobenzylidenethioacetone (Fromm and Höller, *loc. cit.*), the authors have examined the reaction between dibenzylideneacetone and hydrogen sulphide in acid and in ammoniacal solution. Complex compounds are obtained which do not show any marked additive powers, and for which constitutional formulæ are suggested.

Duplodibenzylideneacetoneoxytriamine, $C_{34}H_{35}ON_3$, decomposing at 97°, is an amorphous, yellowish-brown substance obtained by the action of ammonia on an alcoholic suspension of dibenzylideneacetone. It readily loses ammonia when its ethereal solution is treated with hydrogen chloride, whereby the *hydrochloride*, $C_{34}H_{32}ON_2,2HCl$, decomp. 185°, is precipitated, from which ammonium hydroxide liberates *duplodibenzylideneacetoneoxydiamine*, $C_{34}H_{32}ON_2$, which decomposes at 137°. When an alcoholic suspension of dibenzylideneacetone is treated with ammonia, cooled, and then treated with hydrogen sulphide, a yellowish-white precipitate of *duplodibenzylidenethioacetonediamine*, $C_{34}H_{34}N_2S_2$, is obtained, which readily loses hydrogen sulphide and takes up water, yielding *duplodibenzylideneoxythioacetonediamine*, $C_{34}H_{34}ON_2S$, which decomposes at 103—119°, and is best purified through the *hydrochloride*, $C_{34}H_{34}ON_2S,2HCl$. *Duplodibenzylideneacetoneoxytrisulphide*, $C_{34}H_{32}OS_3$, m. p. 110—127° (decomp.), is obtained by saturating an alcoholic suspension of dibenzylideneacetone with hydrogen sulphide, adding a slight excess of alcoholic ammonia, and again passing an excess of hydrogen sulphide. If the solution is saturated with ammonia and submitted to the prolonged action of hydrogen sulphide, *duplodibenzylideneacetonepentasulphide*, $C_{34}H_{32}S_5$, m. p. 201°, is obtained, which crystallises in colourless needles, and is oxidised by potassium permanganate and sulphuric acid in the presence of a little benzene to *duplodibenzylideneacetoneheptaoxytetrasulphide*, $C_{34}H_{32}O_7S_4$, decomp. 160—161°, and *duplodibenzylideneacetonehexaoxytetrasulphide*, $C_{34}H_{32}O_6S_4$, decomp. 130°.

The action of hydrogen chloride, followed by hydrogen sulphide, on an alcoholic suspension of dibenzylideneacetone yields a *substance*, $2C_{17}H_{14}O,3H_2S$, decomp. 150°, or *triplodibenzylideneacetonetetrasulphide*, $C_{51}H_{50}S_4$, m. p. 99—100°.

Speranski's thiomenthene, $C_{20}H_{34}S$, m. p. 50° (Abstr., 1907, i, 627), is precipitated when hydrogen sulphide is passed into a 10% alcoholic solution of menthone saturated with hydrogen chloride.

C. S.

Study of the Benzoin Condensation. THOR EKECRANTZ and ALFR. AHLQVIST (*Arkiv. Kem. Min. Geol*, 1908, 3, No. 13, 1—26). —The benzoin condensation is not general with aromatic aldehydes, the possibility of the reaction depending on the nature of the substituent groups present. The presence of amino-, hydroxy-, or nitro-groups, or of large side-chains, in the aldehyde molecule hinders the reaction, whilst the presence of the substituent group in the meta-position is most favourable to the condensation. With aldehydes containing alkyl- or alkyloxy-groups, the reaction, in general, soon results in an equilibrium between condensation product and unchanged aldehyde. As a secondary reaction, occurs the formation of the acid corresponding with the aldehyde. With nitro-substituted benzaldehydes, large quantities of the acids are formed instead of benzoin, and in the case of *m*- and *p*-nitrobenzaldehydes the ethyl esters of the acids are also formed. With volatile acids, the corresponding cyanohydrins are often formed. Since, in the authors' condensation experiments, the alcohol corresponding with the aldehyde, and formed by the simultaneous oxidation and reduction of the aldehyde, was in no case detected, it is assumed that this alcohol takes part in various reactions, resulting in the formation of resin, which always arises in smaller or larger amount in the reaction between potassium cyanide and substituted aromatic aldehydes. Without invalidating Bredig and Stern's hypothesis that the benzoin condensation is due to catalysis by cyanogen ions (*Zeitsch. Elektrochem.*, 1904, **10**, 582—587), the explanation of the varying behaviour of aromatic aldehydes when treated with potassium cyanide may be found in the acid character of the aldehydes (compare Euler, Abstr., 1906, i, 140). In the case of all aldehydes with which the degree of dissociation is greater than with hydrogen cyanide, for example, the nitrobenzaldehydes, aldehyde salt will be obtained in relatively large quantity, hydrogen cyanide, which is only slightly dissociated, being formed at the same time. Since potassium cyanide in aqueous solution is not only electrolytically dissociated, but also hydrolysed, according to the equation : $KCN + H_2O = KHO + HCN$, the formation of the acid corresponding with the aldehyde may be simply explained as follows : (1) under the influence of dilute alkali a hydrogen atom migrates from one aldehyde molecule to another, giving, for example, $C_6H_4Br{\cdot}CH(OH){\cdot}$ and $C_6H_4Br{\cdot}CO{\cdot}$; (2) these residues take up respectively the hydrogen and hydroxyl formed by hydrolysis, giving $C_6H_4Br{\cdot}CH_2{\cdot}OH$ and $C_6H_4Br{\cdot}CO_2H$. When these acids are formed in large quantities, they give rise to their strongly dissociated potassium salts, which cause a diminution of the cyanogen ions and so prevent the benzoin condensation from taking place. The condensation can therefore only occur with aldehydes which only exhibit a slight tendency to form salts, such as benzaldehyde and its alkyl and alkyloxy-derivatives and halogen derivatives of benzaldehyde and furfuraldehyde. In cases where the substituent group does not alter appreciably the degree of dissociation of the aldehyde, the condensation is considerably retarded by the presence of a side-chain.

In their experiments on the benzoin reaction, the authors dissolved 10—20 grams of aldehyde in four times the quantity of 66% alcohol and heated the mixture, together with an amount of potassium cyanide equal to 10—15% of that of the aldehyde, either (1) in a reflux apparatus on the water-bath for one hour, or (2) in a sealed tube at 60°.

With benzaldehyde, benzoin, benzoic acid, and mandelonitrile were formed.

Of the three tolualdehydes, the para-compound is the slowest to react and the meta-compound the most ready. From *p*-tolualdehyde, *p*-toluic acid is obtained along with the *p*-toluoin. o-*Toluoin*, $C_{16}H_{16}O_2$, crystallises from aqueous alcohol in silky needles, m. p. 79°. *m*-Toluoin could only be obtained as a syrup, oxidation of which with chromic oxide in acetic acid gave m-*tolil*,

$$C_6H_4Me\cdot CO\cdot CO\cdot C_6H_4Me,$$

which crystallises from alcohol in yellow needles, m. p. 103°.

Cuminaldehyde yields cuminoin and cuminic acid. With salicylic aldehyde, no benzoin condensation occurs, the aldehyde undergoing profound decomposition with formation of resin (compare Zincke, *Annalen*, 1883, **216**, 316). *p*-Hydroxybenzaldehyde and vanillin remain almost entirely unchanged, whilst anisaldehyde yields anisoin and anisic acid. Experiments made with 3-methoxy-4-benzyloxybenzaldehyde in order to ascertain the influence of side-chains on the reaction, showed that this compound yields no benzoin.

Benzanisoin, $OH\cdot CHPh\cdot CO\cdot C_6H_4\cdot OMe$, which was prepared by the action of potassium cyanide on a mixture of benzaldehyde and anisaldehyde in 80% alcohol, and is analogous to Fischer's benzofuroin (Abstr., 1880, 798), crystallises from aqueous alcohol in colourless needles, m. p. 105—106°, and dissolves in most organic solvents.

Cuminanisoin, $C_6H_4Pr^{\beta}\cdot CH(OH)\cdot CO\cdot C_6H_4\cdot OMe$, separates from aqueous alcohol in crystals, m. p. 81—82°, and is readily soluble in the ordinary organic solvents.

m-Chlorobenzaldehyde yields small quantities of *m*-dichlorobenzoin, together with *m*-chlorobenzoic acid.

m-Bromobenzaldehyde yields *m*-bromobenzaldehyde cyanohydrin, *m*-bromobenzoic acid, and m-*dibromobenzoin*,

$$C_6H_4Br\cdot CH(OH)\cdot CO\cdot C_6H_4Br,$$

which crystallises from aqueous alcohol in pale yellow needles, m. p. 123—124°, and dissolves readily in the ordinary organic solvents.

From *m*-aminobenzaldehyde, no definite product could be obtained.

T. H. P.

Preparation of Derivatives of Benzanthrone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 200335).—The alkyl derivatives of anthraquinone and α-aminoanthraquinone can be employed in the production of derivatives of benzanthrone (compare Abstr., 1907, i, 324, 943). β-Methylanthranol, produced by the reduction of β-methylanthraquinone with tin and hydrochloric acid, when heated at 140—150° with glycerol and concentrated sulphuric acid gives rise to *methylbenzanthrone*, yellow needles, m. p. 199°.

Dimethylbenzanthrone, yellow needles, m. p. 165°, is similarly obtained from 1 : 3-dimethylanthraquinone (m. p. 159—163°), the latter being first converted into the corresponding oxanthranol. G. T. M.

Constitution and Colour. II. FRIEDRICH KEHRMANN (*Ber.*, 1908, **41**, 3396. Compare this vol., i, 699).—A criticism of K. H. Meyer's views on the halochromism of quinones (this vol., i, 731). J. J. S.

Preparation of Chloroacylaminoanthraquinones. Badische Anilin- & Soda- Fabrik (D.R.-P. 199758).—The aminoanthraquinones when chlorinated or brominated give rise to polyhalogenated derivatives, but when chlorine or chlorine evolving agents react with the acylaminoanthraquinones, the monochloro-derivatives are produced containing the halogen in the ortho- or para-position with regard to the amino-group.

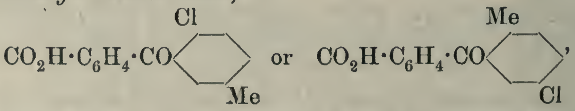
4-*Chloroacetyl*-1-*aminoanthraquinone*, yellow crystals, m. p. 203—204°, obtained by passing chlorine into a glacial acetic acid solution of acetyl-1-aminoanthraquinone and sodium acetate at 80°, gives, on hydrolysis with sulphuric acid, 4-*chloro*-1-*aminoanthraquinone*, red needles, m. p. 179—180°. 4 : 8-*Dichloro*-1 : 5-*diacetyldiaminoanthraquinone*, brown crystals, m. p. above 300°, and 4 : 8-*dichloro*-1 : 5-*diaminoanthraquinone*, red needles with green reflex, were similarly obtained.

1 : 5-Anthraquinonyldiurethane, from 1 : 5-anthraquinone and ethyl chlorocarbonate, when chlorinated in glacial acetic acid gives rise to 4 : 8-*dichloro*-1 : 5-*anthraquinonylurethane*, brown crystals. The preparation of 1-*chloro*-2-*acetylaminoanthraquinone*, yellow leaflets or needles, m. p. 240—241°, 1-*chloro*-2-*aminoanthraquinone*, reddish-brown crystals, m. p. 234—236°, and 1-*chloro*-2-*anthraquinonylurethane*, yellow leaflets m. p. 189—191°, is carried out in a similar manner. G. T. M.

Friedel and Crafts' Reaction. Gustav Heller and Kurt Schülke (*Ber.*, 1908, 41, 3627—3638).—The authors find that in the condensation of phthalic anhydride and benzene in presence of aluminium chloride, a reaction previously studied by Heller (*Zeitsch. angew. Chem.*, 1906, 19, 669), exactly 1 mol. of aluminium chloride, Al_2Cl_6, is required for the condensation of 1 mol. of phthalic anhydride, and suggest that an intermediate compound is formed, thus: $C_8H_4O_3 + Al_2Cl_6 + C_6H_6 \longrightarrow C_8H_4O_3,Al_2Cl_6,C_6H_6 \longrightarrow C_{14}H_9O_3{\cdot}Al_2Cl_5 + HCl$. This reaction has also been extended to the case of other hydrocarbons and some of their derivatives. From benzene and toluene, almost quantitative yields of *o*-benzoylbenzoic and *p*-toluoyl-*o*-benzoic acids were obtained. When the latter is heated on the water-bath with fuming sulphuric acid (20% SO_3), β-methylanthraquinone is obtained in almost colourless needles (Limpricht and Wiegand, Abstr., 1900, i, 498, state that the crystals are usually yellow).

A 97% yield of α-naphthoyl-*o*-benzoic acid is obtained from naphthalene when benzene is used as solvent, and the acid is condensed to naphthanthraquinone by warming with 10 parts of concentrated sulphuric acid at 45—50° (compare Elbs, Abstr., 1886, 1037). This yields a *monosulphonic acid* on treatment with fuming sulphuric acid (20% SO_3). Anthracylbenzoic acid is formed from anthracene, benzene being used as a solvent, but it could not be isolated in the pure state.

p-*Chlorotoluoyl*-o-*benzoic acid*,



prepared from *p* chlorotoluene, crystallises in aggregates of slender needles, m. p. 164—165°. When warmed with fuming sulphuric acid, it condenses to 4-*chloro*-1-*methylanthraquinone*, which forms long, slender, yellow needles, m. p. 164°; on oxidation with permanganate, the acid yields p-*chlorocarboxybenzoyl*-o-*benzoic acid*, $C_{15}H_9O_5Cl$, a crystalline powder, m. p. 234—236°.

When 4-chloro-1-methylanthraquinone is heated under pressure with 66% nitric acid to 195°, it yields 4-*chloroanthraquinone*-1-*carboxylic acid*, crystallising in bundles of yellow needles, m. p. 228—229°.

o-*Chlorotoluoyl*-o-*benzoic acid*, the exact constitution of which was not determined, is prepared from *o*-chlorotoluene; it forms crystalline aggregates, m. p. 182—183°, and on warming with fuming sulphuric acid gives *chloromethylanthraquinone* (Me : Cl = 1 : 2 or 2 : 3), which forms glistening needles, m. p. 213°. By oxidising *o*-chlorotoluoyl-*o*-benzoic acid with permanganate, o-*chlorocarboxybenzoyl*-o-*benzoic acid*, $C_{15}H_9O_5Cl,H_2O$, is produced. This forms long rhombohedra, and loses H_2O above 110°, sinters at 184°, and melts at 188°.

When the chloromethylanthraquinone just described is heated under pressure with 66% nitric acid at 210°, *β-chloroanthraquinonecarboxylic acid* (CO_2H : Cl = 1 : 2 or 2 : 3) is formed. This crystallises in slender, pale yellow, bushy needles, m. p. 280°; the *sodium* salt forms almost colourless needles. On heating above its m. p., the acid loses carbon dioxide, and 2-chloroanthraquinone is left. J. C. C.

The Colour and Affinity for Mordants of Anthraquinone Derivatives. GUSTAV HELLER (*Ber.*, 1908, **41**, 3639—3640).—*β*-Chloroanthraquinonecarboxylic acid and 4-chloroanthraquinone-1-carboxylic acid (preceding abstract), like the other simple derivatives of anthraquinone, are pale yellow. The alkaline solutions, however are almost colourless, and the sodium salts are even paler than the acids. The substances have no affinity for mordants, and it may generally be stated that the affinity for mordants of anthraquinone derivatives is proportional to the intensity of colour of the sodium salts. J. C. C.

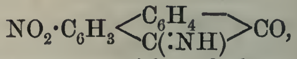
Phenanthrene Series. XXIV. Morpholquinone from Phenanthrene. JULIUS SCHMIDT and JULIUS SÖLL (*Ber.*, 1908, **41**, 3696—3703).—Morpholquinone, 3 : 4-dihydroxyphenanthraquinone, may be obtained from 3-hydroxyphenanthraquinone (Werner, Abstr., 1902, i, 440) by the following stages: nitration, reduction, diazotisation, and boiling with water. A modification of Werner's method of diazotising 3-aminophenanthraquinone is described. Nitric acid reacts with 3-hydroxyphenanthraquinone, yielding a mixture of the isomeric 2- and 4-nitro-derivatives, both of which dissolve readily in sodium carbonate solution. One of these crystallises from glacial acetic acid in yellow needles, and is identical with Werner's product. It has been found possible to obtain a *dinitro*-derivative by the action of nitric acid on 3-hydroxyphenanthraquinone. It crystallises in yellow needles, m. p. 227—228°, and reacts with *o*-phenylenediamine, yielding a *phenanthraphenazine*, m. p. 249°. The morpholquinone is obtained, together with other products, when the mixture of mononitro-derivatives is reduced with tin and hydrochloric acid, the resulting mixture of amino-compounds diazotised, and the diazo-solution boiled.

Morpholquinone can also be prepared from the mother liquors from 3-nitrophenanthraquinone, obtained when 9 : 10-diaminophenanthrene is treated with acetic anhydride and nitric acid (see following abstract). The mother liquor is evaporated, reduced and diazotised, and the resulting diazo-solution boiled. J. J. S.

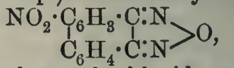
Phenanthrene Series. XXIII. 3-Nitrophenanthraquinone and its Derivatives. JULIUS SCHMIDT and JULIUS SÖLL (*Ber.*, 1908, 41, 3679—3695. Compare Werner, Abstr., 1904, i, 863; Schmidt and Kämpf, Abstr., 1902, i, 757, 797).—Starting with 3-nitrophenanthraquinone, it has been found possible to prepare morpholquinone (compare preceding abstract). A convenient method for the preparation of the 3-nitro-derivative has been worked out, and numerous derivatives have been prepared.

In the case of 3-nitrophenanthraquinonedioxime, it has been found that the replacement of the hydrogen atoms of the oximino-groups by methyl or acetyl produces a weakening in colour (Abstr., 1907, i, 630, 1054), and the same change is observed during anhydride formation (this vol., i, 16).

A modification of Pschorr's method (Abstr., 1902, i, 672) for the preparation of 9 : 10-diaminophenanthrene hydrochloride is described. This salt is best nitrated by first acetylating by boiling with a mixture of acetic anhydride, acetic acid, and the theoretical amount of sodium acetate, and then stirring and heating with concentrated nitric acid in the presence of acetic acid, acetic anhydride, and a small amount (1 gram) of copper. The yield of pure 3-nitrophenanthraquinone is only some 20% of the theoretical.

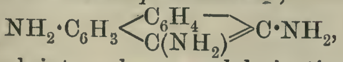
3-*Nitrophenanthraquinone monoimine*, 
$NO_2\cdot C_6H_3<\begin{matrix}C_6H_4\text{—}\\ C(:NH)\end{matrix}>CO$, obtained by shaking 3-nitrophenanthraquinone with alcoholic ammonia for five hours, crystallises from benzene in green prisms with a brassy lustre, and decomposes at 203°. Its benzene solution with hydrogen chloride yields a red *hydrochloride*. When boiled with acetic acid, it is converted back into the quinone.

3-*Nitrophenanthraquinone semicarbazone*, $C_{15}H_{11}O_4N_4$, is extremely unstable, and has m. p. 254° (decomp.). The dioxime, $C_{14}H_9O_4N_3$, crystallises from alcohol in yellowish-red needles, m. p. 200° (decomp.). In the preparation of oximes of nitro-derivatives, it has been found advisable to use granular witherite to neutralise the liberated hydrogen chloride.

The *diacetyl* derivative of the dioxime, $C_{18}H_{13}O_6N_3$, crystallises from benzene in pale yellow plates, m. p. 183° (decomp.). The anhydride of the dioxime, 3-*nitrophenanthrafurazan*, 
$\begin{matrix}NO_2\cdot C_6H_3\cdot C:N\\ C_6H_4\cdot C:N\end{matrix}>O$, is obtained when the dioxime is shaken with benzoyl chloride and sodium hydroxide solution. It crystallises from alcohol in yellow needles, m. p. 230—231°.

The *dimethyl ether* of the dioxime, $C_{16}H_{14}O_2N_2$, obtained by the action of methyl sulphate and concentrated sodium hydroxide solution on a benzene solution of the oxime, crystallises from alcohol in pale yellow needles, m. p. 190—192°.

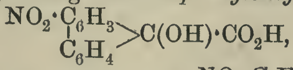
When reduced with an alcoholic solution of stannous chloride, the dioxime yields 3 : 9 : 10-*triaminophenanthrene*,



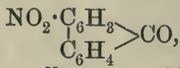
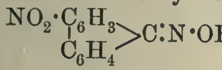
$$NH_2\cdot C_6H_3<\begin{array}{l}C_6H_4-\\C(NH_2)\end{array}>C\cdot NH_2,$$

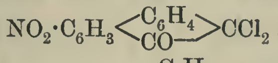
which is transformed into a *hexa-acetyl* derivative, $C_{26}H_{25}O_6N_3$, m. p. 307°, when heated with acetic anhydride and sodium acetate.

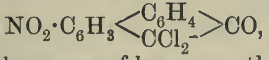
Warm 10% potassium hydroxide solution reacts with 3-nitrophenanthraquinone, yielding 3-*nitrodiphenyleneglycollic acid*,



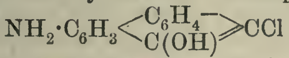
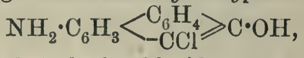
$$\begin{array}{l}NO_2\cdot C_6H_3\\ \quad\ |\\ \quad C_6H_4\end{array}>C(OH)\cdot CO_2H,$$

m. p. 239—240°, and 3-*nitrofluorenone*,  $\begin{array}{l}NO_2\cdot C_6H_3\\ \quad\ |\\ \quad C_6H_4\end{array}>CO$, which crystallises from alcohol in yellowish-brown needles, m. p. 209—210°. The *oxime*,  $\begin{array}{l}NO_2\cdot C_6H_3\\ \quad\ |\\ \quad C_6H_4\end{array}>C{:}N\cdot OH$, also forms yellowish-brown needles, m. p. 240°.

Phosphorus pentachloride reacts with 3-nitrophenanthraquinone, yielding equal quantities of 9 : 9-*dichloro*-3-*nitro*- and 10 : 10-*dichloro*-3-*nitro-phenanthrones*,  $NO_2\cdot C_6H_3<\begin{array}{l}C_6H_4\\CO-\end{array}>CCl_2$ and



$$NO_2\cdot C_6H_3<\begin{array}{l}C_6H_4\\CCl_2-\end{array}>CO,$$

which can be separated by means of benzene ; the α-compound separates in pale yellow plates, m. p. 191—193°. The isomeric β-compound has m. p. 143—145°. When reduced with tin and hydrochloric acid, these two compounds yield the corresponding *chloroaminohydroxyphenanthrenes*,  $NH_2\cdot C_6H_3<\begin{array}{l}C_6H_4-\\C(OH)\end{array}>CCl$ and  $NH_2\cdot C_6H_3<\begin{array}{l}C_6H_4\\-CCl\end{array}>C\cdot OH$, which have been isolated in the form of their hydrochlorides. All attempts to nitrate these chlorohydroxy-compounds proved unsuccessful.

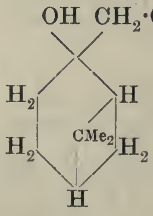
3-Aminophenanthraquinone (Werner, Abstr., 1902, i, 441) yields a *monoxime*, $C_{14}H_{10}O_2N_2$, which crystallises in small, reddish-brown prisms, m. p. 247° (decomp.).

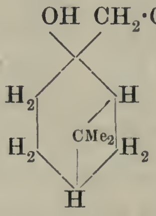
Attempts to obtain nitro-derivatives of the amine proved unsuccessful. With a mixture of acetic acid, acetic anhydride, and nitric acid, the base yields 3-*aminodinitrodiphenic acid*, $C_{14}H_9O_8N_3$, which crystallises from water in colourless plates, m. p. 200—201° (decomp.).

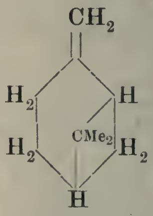
J. J. S.

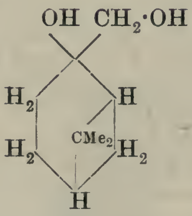
Terpenes and Ethereal Oils. XCVII. Synthesis of Fenchene, β-Pinene, Camphene, and Camphor from Nopinone.

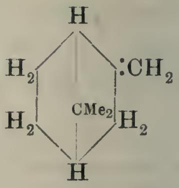
OTTO WALLACH (*Annalen*, 1908, **363**, 1—19. Compare this vol., i, 813).—A previous attempt to prepare β-pinene from nopinone led to the synthesis of a hydrocarbon isomeric with the desired product (Abstr., 1907, i, 1058). Further experiments, however, have now resulted, not only in the synthesis of β-pinene, but also in the discovery of a remarkable intramolecular transformation. The interaction of nopinone, ethyl bromoacetate, and zinc leads to the formation of a hydroxy-ester (I). This was heated directly with potassium hydrogen sulphate, and the resulting unsaturated ester hydrolysed. The terpene, obtained on distillation of the unsaturated acid, is now found to be identical with *Ld*-fenchene (V), which is obtained together with *Ll*-fenchene from *l*-fenchone in the same manner as *Dd*- and *Dl*-fenchenes are formed from *d*-fenchone (Abstr., 1899, i, 65; this vol., i, 809).


(I.)


(II.)


(III.)


(IV.)


(V.)

Ld-Fenchene, on oxidation, yields hydroxyfenchenic acid, m. p. 154°, and on hydration *iso*fenchyl alcohol (Abstr., 1907, i, 1058), m. p. 62—63°, b. p. 202—204°, which on oxidation is converted into *iso*fenchone (compare this vol., i, 809). *iso*Fenchocamphoric acid, m. p. 158—159°, has $[\alpha]_D + 12°$.

On repeating the synthesis from nopinone, there was obtained *Ll*-fenchene, which resembles the *Ld*-isomeride and on hydration forms *iso*fenchyl alcohol, but on oxidation yields hydroxyfenchenic acid, m. p. 135—136°. It is found that the nature of the end-product depends on the manner in which water is split off from ethyl nopinolacetate (I). If the dehydrating agent employed is acetic anhydride, the end-product is a mixture of fenchene and β-pinene, the latter being obtained in greatest amount if the ester is hydrolysed before the dehydration.

Nopinolacetic acid (II), formed by hydrolysis of its ester by means of alkalis, crystallises from light petroleum in prisms, m. p. 83—85°, and is stable towards lead dioxide, but is readily attacked by boiling dilute sulphuric acid, yielding *iso*fenchyl alcohol and an acid substance. When heated with potassium hydrogen sulphate, nopinolacetic acid is converted into an isomeric *acid*, m. p. 85—86°, and a volatile acid, m. p. 174—175°, which may be homodihydrocumic acid. The action of acetic anhydride on nopinolacetic acid leads to the formation of two unsaturated acids, one of which loses carbon dioxide during the reaction and forms *l*-β-pinene (III), b. p. 163—164°, D^{22} 0·8660—0·8675, n_D^{22} 1·4724—1·4749, α $-22° 5'$ to $-22° 20'$; this on oxidation with permanganate forms nopic acid identical with that obtained from natural β-pinene. The second acid is more stable, and decomposes only on distillation, yielding fenchene.

A sparingly soluble *glycol* (IV), crystallising in leaflets, m. p. 75—77° (compare Wagner, Abstr., 1894, i, 610), is obtained together with nopic acid by careful oxidation of the synthetical, as also of the natural, β-pinene. When heated with dilute acids, it yields an *aldehyde*, which has an odour of cuminol, forms a *semicarbazone*, and reduces silver solutions with formation of a silver mirror. When heated at 60° with glacial acetic-sulphuric acid, β-pinene yields terpinene, b. p. 175—180°, and small amounts of *iso*fenchyl acetate, which suggests the presence of traces of fenchene in the synthetical pinene.

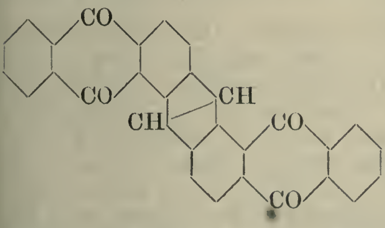
The action of hydrogen chloride on synthetical β-pinene in cooled glacial acetic acid, or anhydrous ethereal solution, leads to the formation of bornyl chloride, m. p. 117—120°, $[\alpha]_D - 22{\cdot}75°$, and dipentene dihydrochloride, m. p. 49—50°.

Camphene, formed from the synthetical *l*-bornyl chloride by the action of sodium acetate and glacial acetic acid at 190—200°, is converted by way of its acetate into *iso*borneol, which on oxidation with chromic acid yields camphor. This series of reactions constitutes the first synthesis of camphor from a compound (nopinone) containing a smaller number of carbon atoms.

It is considered that the first product of the dehydration of nopinolacetic acid (II) is probably β-pinene (III), which undergoes transformation into *Ll*-fenchene, this finally changing into *Ld*-fenchene (V). Such a series of changes must entail a considerable intramolecular transformation, the mechanism of which remains to be investigated.

G. Y.

[Preparation of Complex Anthracene Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 199756).—β-Methylanthraquinone, when heated at 150—170° with alcoholic potash, gives rise to a condensation product, at first present as a dihydroanthracene derivative, but which on oxidation with alkali hypochlorite or atmospheric oxidation yields the annexed *compound*. This substance separates from hot nitrobenzene in golden-yellow crystals, not melting below 360°. The oxidation may also be effected by adding sodium nitrate to the alcoholic potash; the reaction then takes place at 140—150°.



The halogenated derivatives of β-methylanthraquinone give similar condensation products.

G. T. M.

Preparation of Citral Hydrate. PIERRE COULIN (D.R.-P. 198483).—The dihydrodisulphonic derivative of citral was obtained when citral or lemon-grass oil was treated with aqueous sodium sulphite, dilute sulphuric acid being slowly added to neutralise the alkali hydroxide.

The liquid was then cooled to 0°, and treated with 50% sulphuric acid or 30% hydrochloric acid to form an additive compound, from which citral hydrate can be regenerated by the action of alkali hydroxides.
G. T. M.

[Isolation of an Isomeride of Citral Hydrate.] PIERRE COULIN (D.R.-P. 198714. Compare preceding abstract).—The product obtained by the action of acids on the labile dihydrodisulphonic derivative of citral consists of citral hydrate, which is not volatile in steam, and an isomeric compound, which is readily volatile under these conditions. This *isomeride* of citral hydrate has the following properties: b. p. 93·2—95·2°/13 mm., D^{15} 0·964, n_{26} 1·44991, semicarbazone, m. p. 172°, and thiosemicarbazone, m. p. 129°.

When condensed with acetone or methyl ethyl ketone in the presence of alkali hydroxides, this isomeride of citral hydrate gives rise to condensation products, which, by heating with water or a hydrogen sulphite, or treatment with acid, yield perfumes having respectively the formulæ $C_{13}H_{22}O_2$ and $C_{14}H_{24}O_2$.
G. T. M.

[The Condensation of Ketones and Citral Hydrate.] PIERRE COULIN (D.R.-P. 200654).—The condensation of citral hydrate with acetone or methyl ethyl ketone in the presence of sodium peroxide or potassium hydroxide leads to the] production of ψ-ionone hydrate and methyl-ψ-ionone hydrate respectively.
G. T. M.

Preparation of Neutral Esters from Sandal Wood Oil. KNOLL & Co. (D.R.-P. 201369).—*Santolyl succinate* was prepared either by mixing sandal wood oil and succinyl chloride in the presence of pyridine, or by heating the oil with phenyl succinate at 200° in the presence of sodium hydroxide.

Santolyl phosphate is prepared from sandal wood oil, triphenyl phosphate, and sodium hydroxide at 200°. The santolyl esters of other polybasic acids, such as phthalic, citric, and methylenecitric acids, are obtained by similar means.
G. T. M.

Identity of Ilicyl Alcohol and α-Amyrin. ÉMILE JUNGFLEISCH and HENRI LEROUX (*Compt. rend.*, 1908, **147**, 862—864*).—The specimen of ilicyl alcohol obtained by Personne from the bird-lime yielded by the common holly, to which the formula $C_{25}H_{44}O$ was ascribed (Abstr., 1884, 1365), formed colourless needles, m. p. 175°. After several recrystallisations from alcohol, however, it has m. p. 181—181·5°, $[\alpha]_D$ +91·8° (α-amyrin has 181—181·5° and α+91·6° respectively), and the results of its analysis agree closely with the formula, $C_{30}H_{50}O$, of α-amyrin. Further, the acetate prepared either from ilicyl alcohol or from α-amyrin has m. p. 220° and $[\alpha]_D$ +77·9° or +77·0°, whilst the benzoate has m. p. 192° and $[\alpha]_D$ +93·1° or +93·58°, according to the source of preparation.

The identity of the two benzoates is, moreover, rendered conclusive by the fact that both are dimorphous. The acetone solution deposits the benzoate, sometimes separately, sometimes simultaneously, in the form of very long, silky needles, m. p. 170° (on Maquenne block), and as prisms with brilliant facets, m. p. 192° (on Maquenne block). If sown with one form, the solution deposits the whole crop in that form, but both can exist together in solution for several days. The needles, if cooled after melting at 170°, re-melt at 192° (on Maquenne block), which is also the m. p. of the needles if previously heated at 110° for fifteen hours. The needle crystals, if slowly heated, have m. p. 192°, and if melted at 170°, resolidify on continued heating and again melt at 192°. Wyrouboff finds that the prismatic benzoates of the two origins are optically identical. E. H.

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* and *J. Pharm. Chim.*, 1908, **28**, 481—486.

Bakankosin. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1908, **147**, 750—752; *J. Pharm. Chim.*, 1908, [vi], **28**, 433—439) —*Strychnos Bakanko*, from which the authors have isolated (Abstr., 1907, i, 330) the glucoside bakankosin, has been shown by Jumelle to be identical with Baillon's *Strychnos Vacacoua*. The fruit originally employed by the authors was not ripe; they have now examined the seeds from the ripe plant, and find that they also contain the new glucoside, although in less amount (0·92% instead of the 3·6% from the unripe seeds). One part of anhydrous bakankosin dissolves in 3164 parts of ethyl acetate (anhydrous), 55 parts of 95% alcohol, 12 parts of water, or 4 parts of methyl alcohol. Analysis and a cryoscopic determination of the molecular weight show that the glucoside has the formula $C_{16}H_{23}O_8N,H_2O$. Bakankosin is not racemised by baryta, thus being unlike other nitrogenous glucosides. The equation $C_{16}H_{23}O_8N + H_2O = C_6H_{12}O_6 + C_{10}H_{13}O_3N$ is provisionally proposed to represent the hydrolysis effected by emulsin.

Neither the shell of the seed nor the pulp of the fruit contains any glucoside hydrolysed by emulsin. E. H.

Preparation of a Derivative of Gallocyanin. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 198508).—*m*-Chloro-*p*-nitrosodiethylaniline, m.p. 76—77°, a green base, dissolves in alcohol to a yellow solution; its hydrochloride, when condensed with gallaminic acid, gives rise to a gallocyanin derivative analogous to cœlestin-blue, but of a greener shade. G. T. M.

Salts of Guanidine, Dicyanodiamide, and Melamine with Acid Dyes. LEOPOLD RADLBERGER (*Monatsh.*, 1908, **29**, 937—950. Compare Suida, Abstr., 1907, ii, 112).—Guanidine, dicyanodiamide, and melamine behave as monoacidic bases towards the following acid dyes: crystal-ponceau, $C_{20}H_{14}O_7N_2S_2$; ponceau 2 *G*, $C_{16}H_{12}O_7N_2S_2$; chromotrope 2 *R*, $C_{16}H_{12}O_8N_2S_2$; orange IV, $C_{18}H_{15}O_3N_3S$, and orange II, $C_{16}H_{12}O_4N_2S$. The salts formed are analogous to ammonium salts, and are obtained, as a rule, in a crystalline form. The following *salts* were prepared: guanidine with crystal-ponceau, $C_{22}H_{24}O_7N_8S_2,H_2O$, small, reddish-brown needles; with ponceau 2*G*, $C_{18}H_{22}O_7N_8S_2$, red powder; with chromotrope 2*R*, $C_{18}H_{22}O_8N_8S_2$, small, short, brown needles; with orange II, $C_{17}H_{17}O_4N_5S$, yellowish-orange leaflets; with orange IV, $C_{19}H_{20}O_3N_6S$, yellow, monoclinic leaflets.

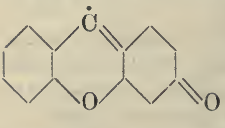
Dicyanodiamide with crystal-ponceau, $C_{24}H_{22}O_7N_{10}S_2,2H_2O$, small, brownish-red needles; with ponceau 2*G*, $C_{20}H_{20}O_7N_{10}S_2$, red powder; with chromotrope 2*R*, $C_{20}H_{20}O_8N_{10}S_2$, brown powder; with orange

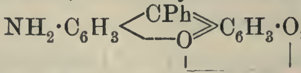
II, $C_{18}H_{16}O_4N_6S$, orange, irregular leaflets; with orange IV, $C_{20}H_{19}O_3N_7S$, orange-yellow prisms.

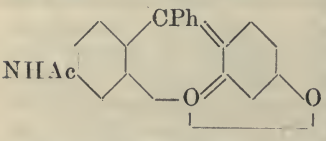
Melamine with crystal-ponceau, $C_{26}H_{26}O_7N_{14}S_2$, red, crystalline powder; with orange II, $C_{19}H_{18}O_4N_8S$, small, pale yellow crystals.

W. H. G.

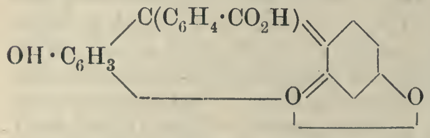
Carboxonium Dyes. I. The Chromogen of Fluorescein and the Simplest Rosamine. FRIEDRICH KEHRMANN and O. DENGLER (*Ber.*, 1908, **41**, 3440—3447).—Following Möhlau and Koch (Abstr., 1895, i, 46), the authors give the name "fluorone" to the annexed group, but prefer the ortho-quinonoid structure depicted in the annexed formulæ.

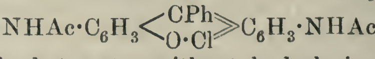


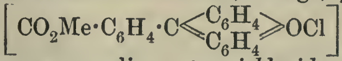
When *m*-acetylaminophenol and benzotrichloride are heated at 150—160° in the presence of nitrobenzene, several substances are obtained, from which, after somewhat complicated treatment, two acetylated bases are isolated and separated from each other by alcohol. The less soluble one is *acetylaminophenylfluorone* (annexed constitution), m. p. above 360°, which crystallises in tufts of red needles, is insoluble in alkalis, and gives strongly fluorescent solutions in alcohol, glacial acetic acid, benzene, or warm dilute mineral acids. In concentrated sulphuric acid it gives a yellow solution with a strong green fluorescence, which remains unchanged by the addition of ice. By hydrolysis by moderately concentrated hydrochloric acid and boiling alcohol, it yields the chloride of the base, which crystallises in red leaflets with a blue reflex. The *base*,  $NH_2\cdot C_6H_3<^{CPh}_{-O}\geqslant C_6H_3\cdot O$, liberated by excess of ammonium hydroxide, has m. p. 305°, crystallises in dark red needles, forms orange-red salts, and by the elimination of the amino-group yields *phenylfluorone*, m. p. 204°, which forms orange-yellow crystals, is insoluble in alkalis or dilute mineral acids, and gives fluorescent solutions. The substance is the chromogen of fluorescein, and shows a striking analogy to *apo*safranone, oxazone, and thiazone.



Hydroxyphenylfluorone, obtained by replacing the amino-group of the preceding base by hydroxyl, is identical with Doebner's resorcinolbenzein (*Annalen*, 1878, **217**, 234), and shows a remarkable similarity in its colour phenomena to fluorescein, which, as its carboxylic acid, must have the annexed constitution (compare R. Meyer and Hoffmeyer, Abstr., 1892, 970.)



The other product isolated from the substances obtained from *m*-acetylaminophenol and benzotrichloride is *diacetylphenorosamine*, the chloride of which,  $NHAc\cdot C_6H_3<^{CPh}_{O\cdot Cl}\geqslant C_6H_3\cdot NHAc$, forms a yellow, fluorescent solution in hot water without hydrolysis. By treatment with ammonium hydroxide, the chloride is changed to a magenta-red, unstable colour base, which is spontaneously transformed to a colourless, stable form, from which dilute acids regenerate yellow salts. By hydrolysis, the simplest rosamine is obtained as a yellowish-red, extremely fluorescent dye. C. S.

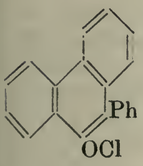
Quinonoid Ester Salts of Fluoran. Arthur G. Green and Percy E. King (*Ber.*, 1908, **41**, 3434—3440. Compare Abstr., 1906, i, 670; 1907, i, 933).—In support of their ortho-quinonoid formula for the oxonium salts of quinolphthalein derivatives, the authors have prepared similar oxonium salts of the esters of fluoran and of 2:7-dimethylfluoran. The substances are unstable and extremely soluble, and their isolation is only possible in the form of the tin or zinc double chlorides. When hydrogen chloride is passed into hot methyl alcohol containing fluoran and stannic chloride, orange, prismatic crystals of the *stannichloride*,  $\left[CO_2Me\cdot C_6H_4\cdot C\lessdot{}^{C_6H_4}_{C_6H_4}\gtrdot OCl\right]_2,SnCl_4$, are obtained on keeping. The corresponding *stannichloride* of the ethyl ester crystallises in large, yellow prisms, containing 1 mol. EtOH. The *stannichloride* of the oxonium chloride of the methyl ester of 2:7-dimethylfluoran contains equal molecular quantities of the oxonium and of the metallic chloride; this appears to depend on the solubility, for zincichlorides containing one or two mols. of the oxonium chloride to one mol. of zinc chloride have been prepared, namely,

$$C_{21}H_{16}OCl(CO_2Me),ZnCl_2$$

and $[C_{21}H_{16}OCl(CO_2Me)]_2.ZnCl_2$.

2:7-*Dichlorofluoran*, $C_{20}H_{10}O_3Cl_2$, m. p. 256—258°, is obtained by condensing phthalic anhydride and *p*-chlorophenol with concentrated sulphuric acid at 150—160°. The halogen atoms are not readily displaced, and the substance, as also the corresponding dinitrofluoran, does not readily esterify under the preceding conditions. C. S.

Dibenzopyronium. Hermann Decker and Heinrich Felser (*Ber.*, 1908, **41**, 3755—3757. Compare Abstr., 1907, i, 1064).—It has been found possible to prepare derivatives of dibenzopyronium, the oxygen isologue of phenanthridine.



9-*Phenyldibenzopyronium* may be obtained by the method of Bünzly and Decker (Abstr., 1904, i, 912), namely, by the action of magnesium phenyl bromide on diphenylmethylolid (compare Graebe and Schestakoff, Abstr., 1895, i, 372). The *carbinol base* is not such a strong base as 9-phenylxanthonium carbinol; the *chloride* (annexed formula) dissolves in hydrochloric acid, forming a yellow solution without fluorescence; the *ferrichloride*, $C_{19}H_{13}OCl,FeCl_3$, crystallises in lemon-yellow leaflets, m. p. 163°. W. H. G.

Preparation of 3-Oxythionaphthen. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 200200).—Methyl *o*-methylthiolbenzoate, $SMe\cdot C_6H_4\cdot CO_2Me$, needles, m. p. 67°, volatile in steam, produced by alkylating *o*-methylthiolbenzoic acid, $SMe\cdot C_6H_4\cdot CO_2H$, m. p. 168—169°, or the corresponding sodium, potassium, or calcium methylthiolbenzoate, when heated with sodium and potassium hydroxides (equal mols.) at 200° gives rise to 3-oxythionaphthen;

this condensation takes place even more readily when some sodium or potassium ethoxide is present in the fusion. G. T. M.

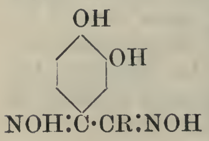
Preparation of a Dihydroxythionaphthencarboxylic Acid. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 200202).—5-Sulphoanthranylthiolacetic acid,

$$SO_3H\cdot C_6H_3(CO_2H)\cdot NH\cdot S\cdot CH_2\cdot CO_2H,$$

prepared from 5-sulphoaniline-2-carboxylic acid, yields a monopotassium salt; this compound when heated with alkali hydroxides, first at 130—140° and then at 160—185°, gives rise to a yellow fusion product, which, when dissolved in water and acidified, furnishes a *dihydroxythionaphthen-2-carboxylic acid.* On boiling with water, this acid yields a dihydroxythionaphthen, needles, m. p. 198°.

G. T. M.

[Preparation of Bases of the Adrenaline Series.] Chemische Fabrik auf Actien (vorm. E. Schering) (D.R.-P. 201245).—The acid reduction with sodium, potassium, or aluminium amalgams of 3 : 4-dihydroxyphenylglyoxime and the 3 : 4-dihydroxyphenylalkylglyoximes of the annexed general formula leads to the production of bases having a very intense hæmostatic action, but which are less toxic than adrenaline. Neither the bases nor their salts have yet been isolated in a pure state.



G. T. M.

Preparation of a Double Compound of Caffeine and Lithium Benzoate. Peter Bergell (D.R.-P. 199108).—A crystalline double compound, $2C_6H_5\cdot CO_2Li,C_8H_{10}O_2N_4$, is obtained in needles by evaporating below 50° under reduced pressure an aqueous solution of caffeine and lithium benzoate. G. T. M.

Solubility of True and False Tannates of Quinine. F. Muraro (*Gazzetta*, 1908, **38**, ii, 507—511).—A reply to Biginelli's criticisms (this vol., i, 562) on the author's previous paper (this vol., i 451). T. H. P.

Preparation of α-Bromo*iso*valerylquinone. Knoll & Co. (D.R.-P. 200063).—Quinine or its salts, when heated for three hours at 120° with α-bromo*iso*valeryl chloride or bromide, gives rise to *α-bromo-isovalerylquinine,* an amorphous, yellow substance, dissolving in alcohols and in acids, but less soluble in benzene, toluene, light petroleum, or ether. From acid solution, it is precipitated by potassium mercuri-iodide. G. T. M.

Synthesis of Polypeptides. XXVII. I. Derivatives of Histidine. Emil Fischer and Lee H. Cone (*Annalen*, 1908, **363**, 107—117. Compare this vol., i, 773).—So far there has been described only one dipeptide, histidylhistidine, derived from histidine, which itself is widely spread amongst the natural proteins. It was of special interest, therefore, to undertake the synthesis of mixed peptides derived from this amino-acid, especially as these may be expected to occur amongst the degradation products of the proteins.

The combination of *l*-leucine with histidine is described in the present paper. As oxyhæmoglobin contains considerable quantities of *l*-leucine and histidine, which are present probably as a mixed dipeptide, and as *l*-leucyl-*l*-histidine is stable towards concentrated hydrochloric acid, it was hoped to find this dipeptide amongst the products of the action of concentrated hydrochloric acid on oxyhæmoglobin. In this the authors have been unsuccessful, as also, so far, in attempts to prepare the isomeride, *l*-histidyl-*l*-leucine. It is found that histidine hydrochloride is stable towards cold phosphorus pentachloride and acetyl chloride. Experiments with formylhistidine, which is described, are in progress.

d-*α-Bromo*iso*hexoyl*-l-*histidine methyl ester*,

$$C_4H_9\cdot CHBr\cdot CO\cdot NH\cdot CH(C_4H_5N_2)\cdot CO_2Me,$$

prepared from *d*-*α*-bromo*iso*hexoyl chloride and histidine methyl ester (Fischer and Suzuchi, Abstr., 1906, i, 73) in chloroform solution, crystallises from ethyl acetate in strongly refracting, colourless, hexagonal plates, m. p. 175° (corr.), dissolves in dilute mineral acids, and is reprecipitated by sodium carbonate.

d-*α-Bromo*iso*hexoyl*-l-*histidine*, $C_{12}H_{18}O_3N_3Br$, prepared by hydrolysis of the ester with *N*-sodium hydroxide at the laboratory temperature and evaporation of the product after neutralisation with sulphuric acid, separates from water in crystals, m. p. 118° (corr.), has an acid reaction in aqueous solution, and gradually becomes yellow when dissolved in alkalis.

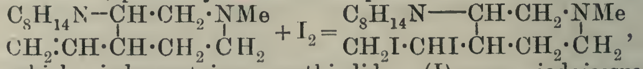
l-*Leucyl*-l-*histidine*, $C_4H_9\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(C_4H_5N_2)\cdot CO_2H$, is best prepared by the action of 25% aqueous ammonia on the preceding bromo-compound at 25°. It separates from water in prisms or plates containing H_2O, loses H_2O at 100°/15—20 mm., when anhydrous has m. p. 178° (corr.) (decomp.), has a strong alkaline reaction in aqueous solution, gives a colourless precipitate with mercuric chloride solution and a red coloration with *p*-diazobenzenesulphonic acid, and becomes dark coloured when boiled with dilute bromine water; these reactions show that the iminazole nucleus of the histidine is present unchanged in the dipeptide. The dipeptide is soluble in dilute acids and alkalis; the acid solutions give a heavy precipitate with phosphotungstic acid. The *copper* salt, $C_{12}H_{18}O_3N_4Cu,4H_2O$, formed by boiling the aqueous solution of the dipeptide with precipitated copper oxide, or by adding copper sulphate to the solution of the dipeptide in sodium hydroxide, is obtained in deep violet-blue crystals, which lose $4H_2O$, becoming lilac at 100°/15—20 mm. over phosphoric oxide, and dissolve in alcohol, forming a violet-blue solution. Whilst it is stable towards cold concentrated mineral acid, the dipeptide is hydrolysed completely in twenty-four hours by 20% hydrochloric acid at 100°, yielding *l*-leucine and *l*-histidine.

Formyl-l-*histidine*, $C_7H_9O_3N_3$, formed by heating histidine with anhydrous formic acid on the water-bath and evaporating the solution under 15—20 mm. pressure, crystallises from aqueous-methyl alcohol in slender needles, m. p. 203° (corr.), is readily soluble in water, slightly so in methyl alcohol, but almost insoluble in other organic solvents, has an acid reaction in aqueous solution, and gives a deep red coloration with *p*-diazobenzenesulphonic acid, which points to the formyl group as having entered into combination with the amino-group of the histidine. G. Y.

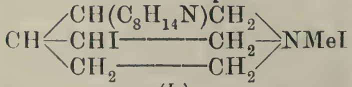
Action of Ozone on Thebaine. J. D. RIEDEL (D.R.-P. 201324).—Thebaine hydrochloride in 10% aqueous solution is treated with ozonised oxygen at the ordinary temperature until the product is soluble in alkali hydroxides. The ethereal extract of the solution, when dried with potassium carbonate and concentrated, furnishes a *compound*, $C_{19}H_{21}O_5N$, which crystallises in needles or leaflets, m. p. 125—126°. This oxidation product still contains two methyl groups, and loses one of these by alkaline hydrolysis; it has probably the formula $C_{15}H_{15}ON(CO_2Me)(CO)\cdot OMe$. The substance is readily soluble in water, ethyl acetate, and alcohol.

G. T. M.

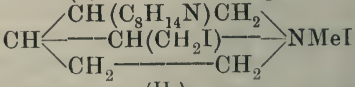
Sparteine. New Method of Ring-formation of α-Methylsparteine by the Action of Iodine. AMAND VALEUR (*Compt. rend.*, 1908, **147**, 864—867).—Although the α-methylsparteine obtained by Moureu and Valeur (this vol., i, 44) by heating methylsparteinium hydroxide is certainly an unsaturated base, since it reduces a cold sulphuric acid solution of potassium permanganate, it is not reduced by sodium and ethyl or amyl alcohol, or by tin and hydrochloric acid. It combines with iodine, however, forming *di-iodo-α-methylsparteine*, $C_{15}H_{25}N_2MeI_2$, m. p. 177—178°, which does not behave as a simple additive product, has a very feebly alkaline reaction, and when treated in aqueous solution with freshly prepared silver oxide gives a strongly alkaline liquid, from which the di-iodide is re-formed by addition of potassium iodide. The latter observation indicates that the new compound is a quaternary ammonium iodide, and therefore must be the methiodide of an iodo-base. In the action of iodine, probably the additive product is first formed, thus:



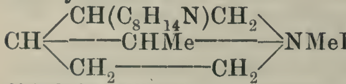
from which iodosparteine methiodide (I) or iodo*iso*sparteine



(I.)



(II.)

methiodide (II) can be formed according to which iodine atom wanders to the nitrogen. Whilst zinc and water or zinc and acetic acid reduce the di-iodide, giving α-methylsparteine only, phosphorus and hydriodic acid at 120° transform it into *iso*sparteine methiodide, , which supports the view that the new di-iodide should be represented by formula (II). It is possible, however, that the *iso*sparteine methiodide is formed by isomeric change from the α-methylsparteine under the influence of hydrogen iodide. These results confirm the analogy which exists between the two bases dimethylpiperidine and α-methylsparteine (compare Willstätter, Abstr., 1900, i, 249; Valeur, this vol., i, 736). E. H.

Iodine Derivatives of Strychnine and Brucine. Józef Buraczewski and Tad. Koźniewski (*Bull. Acad. Sci. Cracow*, 1908, 644—649).—By the addition of a somewhat concentrated solution of iodine in carbon disulphide to a hot alcoholic solution of strychnine or brucine, di-iodo-derivatives are precipitated, from which the alkaloids are regenerated by alcoholic alkalis; it is not yet determined whether the compounds are produced by addition or by substitution.

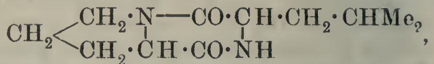
The *strychnine* derivative, $C_{21}H_{22}O_2N_2I_2$ or $C_{21}H_{20}O_2N_2I_2$, m. p. 196—197°, forms red crystals; after prolonged boiling with alcohol, the solution deposits ruby-red crystals of a *substance*, $C_{21}H_{23}O_2N_2I_3$, m. p. 253—254°, which seems to be identical with Jörgensen's periodide (*J. pr. Chem.*, 1870, [i], 2, 434). The *brucine* derivative, $C_{23}H_{26}O_4N_2I_2$ or $C_{23}H_{24}O_4N_2I_2$, m. p. 222·5°, is converted, after prolonged boiling with alcohol, into a ruby-red, crystalline substance, m. p. 251—252°. C. S.

A New Base from Putrefying Pancreas. D. Ackermann (*Zeitsch. physiol Chem.*, 1908, **57**, 28—29).—A new base, *viridinine*, $C_8H_{12}O_3N_2$, has been isolated from ox pancreas which had been allowed to undergo decomposition by exposure to the atmosphere during two months. It may be extracted by Kutscher's method, and is found in the same fraction as δ-aminovaleric acid, but may be separated from this by means of the slight solubility of its aurichloride or platinichloride. The *hydrochloride* forms glistening, green needles, only moderately soluble in cold water, and when heated produces yellow vapours with an aromatic odour. The *aurichloride*, $C_8H_{12}O_3N_2,HAuCl_4$, forms glistening, blackish-green or blackish-yellow plates, or, after recrystallisation, brownish-black needles, m. p. 176° (decomp.). The *platinichloride*, $(C_8H_{12}O_3N_2)_2,H_2PtCl_6$, has an intense yellow colour, and has m. p 212—216° (decomp.). J. J. S.

Synthesis of Polypeptides. XXVII. 2. Derivatives of Proline. [Pyrrolidine-2-carboxylic Acid]. Emil Fischer and Georg Reif (*Annalen*, 1908, **363**, 118—135).—Leven and Beatty isolated from the product of the tryptic digestion of gelatin a prolylglycine anhydride which, on hydrolysis, yields glycine and optically active proline (Abstr., 1906, i, 718). As other similar substances may be formed by the decomposition of proteins, it was thought of interest to study the synthesis of polypeptides derived from active proline.

l-Proline, prepared from gelatin, is best purified by conversion into the *copper* salt, $C_{10}H_{16}O_4N_2Cu$, which crystallises from alcohol in dark blue, rhombic prisms, and when treated with hydrogen sulphide in hot aqueous solution yields proline, $[\alpha]_D^{20}$ − 76·7°. When treated with acetyl chloride, cooled by ice, and then with phosphorus pentachloride, *l*-proline forms l-*prolyl chloride hydrochloride*, $C_4H_8N\cdot COCl,HCl$. This, when treated with glycine ethyl ester in chloroform solution at − 10°, and then, after removal of the chloroform and excess of glycine ester, with dilute sodium ethoxide, yields prolylglycine anhydride and a brown oil. The anhydride, on extraction with boiling ethyl acetate or acetone, is obtained in microscopic leaflets, m. p. 213° (182—183°: Levene and Beatty, *loc. cit.*), $[\alpha]_D^{20}$ − 216·2° to − 217·4°, has a bitter taste, and does not give a blue coloration when boiled in aqueous solution with copper oxide.

Prolyl-leucine anhydride,



$$CH_2<\begin{matrix}CH_2\cdot N\text{---}CO\cdot CH\cdot CH_2\cdot CHMe_2\\ CH_2\cdot CH\cdot CO\cdot NH\end{matrix},$$

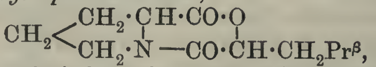
prepared in the same manner from *l*-prolyl chloride hydrochloride and *l*-leucine ethyl ester, crystallises from water in microscopic leaflets, m. p. 160° (corr.), $[\alpha]_D^{20}$ $-142{\cdot}6°$ to $-143{\cdot}4°$. When boiled with 20% hydrochloric acid, the anhydride yields proline, $[\alpha]_D^{20}$ $-56{\cdot}9°$, and leucine, $[\alpha]_D^{20}$ $+10{\cdot}1°$; hence racemisation must have taken place to the extent of one-third of the substance during the hydrolysis.

d-*α-Bromo*iso*hexoyl*-l-*proline*, $CHMe_2\cdot CH_2\cdot CHBr\cdot CO\cdot C_4H_7N\cdot CO_2H$, formed by the action of *d*-bromo*iso*hexoyl chloride and sodium hydroxide on *l*-proline, separates from acetone in crystals, m. p. 158° (corr.) (decomp.). When treated with concentrated aqueous ammonia at 25°, it is converted into *α-hydroxy*iso*hexoyl*-l-*prolinamide*,

$$C_4H_9\cdot CH(OH)\cdot CO\cdot C_4H_7N\cdot CO\cdot NH_2,$$

which is formed also by the action of liquid ammonia on bromo*iso*hexoylproline. It crystallises from water in prisms, m. p. 123—124° (corr.), evolves ammonia at about 140°, $[\alpha]_D^{20}$ $-78{\cdot}3°$ to $-78{\cdot}6°$, and yields ammonia when boiled with sodium hydroxide.

*α-Hydroxy*iso*hexoyl*-l-*prolinolactone*,



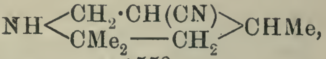
$$CH_2<\begin{matrix}CH_2\cdot CH\cdot CO\cdot O\\ CH_2\cdot N\text{---}CO\cdot CH\cdot CH_2Pr^{\beta}\end{matrix},$$

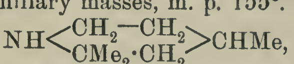
formed when the amide is heated at 140—145°, or when *d*-α-bromo*iso*hexoyl-*l*-proline is treated with sodium hydroxide at the ordinary temperature, and, after twenty-four hours, is neutralised with hydrochloric acid and evaporated, crystallises from water in thin needles, m. p. 164° (corr.), $[\alpha]_D^{20}$ $-166{\cdot}8°$, has a slightly bitter taste, and behaves towards alkalis and acids in the ordinary manner of the lactones.

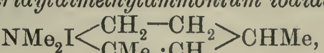
The substance described previously (Abstr., 1904, i, 917) as *i*-leucylproline is now found to be *i*-hydroxy*iso*hexoyl prolinamide; on hydrolysis with acids, it yields ammonia, *dl*-α-hydroxy*iso*hexoic acid, and *dl*-proline. The anhydride, previously termed leucylproline anhydride (*loc. cit.*), is *i*-hydroxy*iso*hexoylproline anhydride; it has m. p. 124° (corr.). G. Y.

New Isomerides of Coniine and other Hydrogenated Bases. Icilio Guareschi (*Atti R. Accad. Sci. Torino*, 1908, **43**, 1095—1099. Compare following abstract).—No isomeride of coniine or other alkyl derivative of piperidine is known in which two alkyl groups are united to one and the same carbon atom. Such a derivative, namely, 2 : 2 : 4-trimethylpiperidine, should be obtainable from 5-cyano-2 : 2 : 4-trimethyldihydro-6-pyridone (compare Abstr., 1894, i, 484) by reduction with sodium and alcohol, whilst cyano-1-methylpyridones should yield the corresponding 1-methylpiperidines, 5-cyano-2 : 3 : 4-trimethyl-6-pyridone, and 2 : 3 : 4-trimethylpiperidine. In the last case, profound reduction by means of zinc dust gives 2 : 3 : 4-trimethylpyridine (compare Abstr., 1900, i, 558). Reduction of 3 : 5-dicyano-2 : 6-diketo-4-methyl-4-ethylhexahydropyridine should also give an isomeride of coniine, 4-methyl-4-ethylpiperidine. T. H. P.

New Isomeride of Coniine from 5-Cyano-2 : 2 : 4-trimethyldihydro-6-pyridone. Giovanni Issoglio (*Atti R. Accad. Sci. Torino*, 1908, **43**, 1100—1121. Compare preceding abstract).—The author has investigated the products of reduction of 5-cyano-2 : 2 : 4-trimethyldihydro-6-pyridone (compare Guareschi, Abstr., 1893, i, 484) by means of (1) sodium and ethyl alcohol, and (2) sodium and amyl alcohol. The first method of reduction yields 2 : 2 : 4-trimethylpiperidine and 5-cyano-2 : 2 : 4-trimethylpiperidine (?) in small quantities, whilst the use of amyl alcohol leads to the formation of (1) 2 : 2 : 4-trimethylpiperidine, (2) a hexamethyldipiperidine, as the result of the condensing action of the excess of sodium on the preceding compound, and (3) 2 : 2 : 4-trimethylnipecotinic acid, derived from the complete hydrogenation of the pyridone and the hydrolysis of the cyanogen residue. The normal reduction of the cyanogen group to $\cdot CH_2\cdot NH_2$ by means of sodium and alcohol is not observed in this case.

5-*Cyano*-2 : 2 : 4-*trimethylpiperidine* (?), 
$\mathrm{NH}<\begin{array}{l}\mathrm{CH_2\cdot CH(CN)}\\\mathrm{CMe_2—CH_2}\end{array}>\mathrm{CHMe}$, crystallises from water in mammillary masses, m. p. 155°.

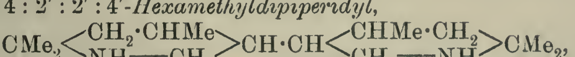
2 : 2 : 4-*Trimethylpiperidine*, 
$\mathrm{NH}<\begin{array}{l}\mathrm{CH_2—CH_2}\\\mathrm{CMe_2\cdot CH_2}\end{array}>\mathrm{CHMe}$, is a mobile liquid, b. p. 148°, D^{15} 0·832, has an intense alkaline reaction, and forms white fumes with hydrogen chloride; with copper sulphate it gives a blue precipitate, soluble in excess of reagent, and with Nessler's reagent, a white precipitate. The aqueous solution of its hydrochloride gives precipitates with the ordinary alkaloidal reagents. The *platinichloride*, $(C_8H_{17}N)_2,H_2PtCl_6$, forms orange-red, mammillary masses, m. p. 215—216° (decomp.). The *aurichloride*, $C_8H_{17}N,HAuCl_4$, crystallises in yellow prisms, m. p. 135°. With methyl iodide, it gives 2 : 2 : 4-*trimethylpiperidyldimethylammonium iodide*,



$$\mathrm{NMe_2I}<\begin{array}{l}\mathrm{CH_2—CH_2}\\\mathrm{CMe_2\cdot CH_2}\end{array}>\mathrm{CHMe},$$

which separates from a mixture of alcohol and ether as a white, crystalline powder, m. p. 266° (decomp.).

2 : 2 : 4 : 2′ : 2′ : 4′-*Hexamethyldipiperidyl*,



$$\mathrm{CMe_2}<\begin{array}{l}\mathrm{CH_2\cdot CHMe}\\\mathrm{NH——CH_2}\end{array}>\mathrm{CH\cdot CH}<\begin{array}{l}\mathrm{CHMe\cdot CH_2}\\\mathrm{CH_2——NH}\end{array}>\mathrm{CMe_2},$$

b. p. 266—267°/745 mm. and 237°/40 mm., D^{15} 0·869, has an odour resembling that of nicotine, and exhibits intense alkaline properties. Its *platinichloride*, $C_{16}H_{32}N_2.H_2PtCl_6,3H_2O$, forms orange-yellow laminæ, m. p. 262° (decomp.); its *picrate*, pale yellow needles, m. p. 230°; its *aurichloride*, $C_{16}H_{32}N_2,2HAuCl_4$, separates as a yellow powder, which changes gradually into laminæ, m. p. 183—184°; its *mercurichloride*, $C_{16}H_{32}N_2,2HCl,HgCl_2$, forms short, colourless prisms, m. p. 270° (decomp.). When heated in a sealed tube with methyl iodide (2 mols.), the base (1 mol.) forms the *compound*, $C_8H_{16}N\cdot C_8H_{15}NMe_2I$, which is obtained as a dense oil, and, when evaporated with hydrochloric acid, gives a syrupy residue, from which the *platinichloride*,

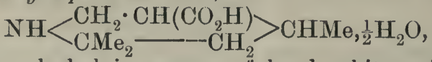
$$C_{16}H_{31}N_2Me_2Cl,HCl,PtCl_4,$$

m. p. 214°, is obtained. With 4 mols. of methyl iodide in methyl alcohol, the base (1 mol.) gives the *compound*,

$$NMe_2I\cdot C_8H_{15}\cdot C_8H_{15}\cdot NMe_2I,$$

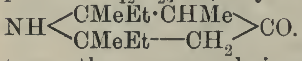
which crystallises from methyl alcohol in monoclinic laminæ, m. p. 236—237°; the action of moist silver oxide gives the corresponding hydroxide, which is an energetic base, and in presence of hydrochloric acid gives the *platinichloride*, $C_{16}H_{30}N_2Me_4Cl_2,PtCl_4$, m. p. 227—228°.

2 : 2 : 4-*Trimethylnipecotinic acid*,



$$NH<\begin{matrix}CH_2\cdot CH(CO_2H)\\ CMe_2\text{———}CH_2\end{matrix}>CHMe,\tfrac{1}{2}H_2O,$$

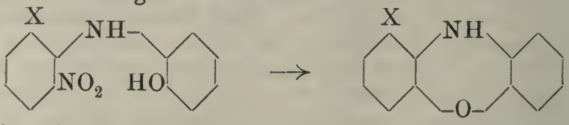
crystallises from alcohol in groups of hard, white prisms, m. p. 123° (efferves.). T. H. P.

Preparation of Basic Compounds from Methyl Ethyl Ketone. WILHELM TRAUBE (D.R.-P. 200203).—Acetone absorbs much more ammonia than its homologues, giving rise to diacetoneamine, and in smaller proportion, triacetoneamine; but by saturating an alcoholic solution of methyl ethyl ketone, a basic condensation product, $C_{12}H_{23}ON$, may be obtained, having probably the constitution  $NH<\begin{matrix}CMeEt\cdot CHMe\\ CMeEt\text{—}CH_2\end{matrix}>CO$. In accordance with this view of its structure, the compound is called either 2 : 3 : 6-*trimethyl*-2 : 6-*diethyl*-4-*piperidone* or *trimethyldiethylketoneamine*. It is a yellow oil, b. p. 247°/740 mm. and 157—159°/30 mm.; hydrochloride, m. p. 128°; *sulphate*, decomposes at 188°; *nitrate*, m. p. 169—172°; *hydrogen oxalate*, m. p. 183°. Another basic product, b. p. 104°/30 mm., is also formed in this condensation, and is separated from the preceding compound by means of its more soluble oxalate. G. T. M.

Preparation of Anthracene Derivatives containing Nitrogen. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 199713).—It was shown previously (compare this vol., i, 699) that the acetyl derivatives of the secondary α-aminoanthraquinones, when condensed with the aid of alkalis, gave rise to products of the pyridone series. Similarly, sulphonated pyridones are obtained from the sulphonic acids of acetyl-α-methylaminoanthraquinone.

G. T. M.

Preparation of Phenoxazines. ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 200736).—The substituted nitrohydroxydiphenylamines having the constitution:

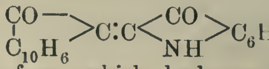


readily give rise to phenoxazines; this reaction, however, does not take place in the absence of a substituent in position 6, denoted by X.

5-*Nitrophenoxazine*, reddish-violet needles, m. p. 165°, was obtained from 2 : 6-dinitro-2′-hydroxydiphenylamine by warming with 5% aqueous sodium hydroxide. The patent contains a description of six phenoxazine-carboxylic and -sulphonic acids derived from carboxy- and sulpho-nitro-2-hydroxy-diphenylamines. G. T. M.

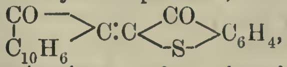
Some Unsymmetrical Analogues of Indigotin. ARMIN GROB (*Ber.*, 1908, 41, 3331—3334).—The two dyes referred to below have been recently described by Bezdrik and Friedländer (this vol., i, 674), but the author claims priority, as a patent for their preparation had been applied for by the Basler Chemische Fabrik in January—June, 1907.

8-Oxy-7-indoxylacenaphthene,



$\begin{array}{l}CO-\\ |\\ C_{10}H_6\end{array}\!>C{:}C<\!\begin{array}{c}CO\\ NH\end{array}\!>C_6H_4$, gives an additive product with bromine, from which hydrogen bromide is expelled on heating, leaving a violet bromine-substituted dye. The solution of the leuco-compound of 8-oxy-7-indoxylacenaphthene is violet.

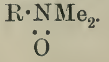
8-Oxy-7-oxythionaphthenylacenaphthene,



$$\begin{array}{l}CO-\\ |\\ C_{10}H_6\end{array}\!>C{:}C<\!\begin{array}{c}CO\\ S\end{array}\!>C_6H_4,$$

may be prepared by condensing *o*-carboxyphenylthioglycollic acid with acenaphthenequinone in acetic anhydride solution. It gives a bromine additive compound, and the solution of its leuco-compound is reddish-violet. J. C. C.

Amino-oxides of Leuco-bases of the Di- and Tri-phenylmethane Series. EUGEN BAMBERGER and LEO RUDOLF (*Ber.*, 1908, 41, 3290—3315).—The authors have investigated the action of hydrogen peroxide and of Caro's acid on tetramethyldiaminodiphenylmethane, tetramethyldiaminotriphenylmethane, and hexamethyltriaminotriphenylmethane, and find that oxides are formed analogous to those obtained from dimethylaniline, etc., thus:



$R{\cdot}\underset{\overset{\cdot\cdot}{O}}{NMe_2}$.

4 : 4′-*Tetramethyldiaminodiphenylmethane dioxide*,

$$NMe_2O{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}NMe_2O,2H_2O,$$

is most conveniently prepared by the use of Caro's acid. It forms hard, colourless, glistening needles, m. p. 147°. When heated, it evolves vapours of formaldehyde. The aqueous solution has a faint alkaline reaction, and does not reduce Fehling's solution or oxidise potassium iodide. When exposed for three months over concentrated sulphuric acid at 12—15 mm. pressure, the anhydrous compound, m. p. 156°, is formed. The *picrate*,

$$CH_2[C_6H_4{\cdot}NMe_2(OH){\cdot}O{\cdot}C_6H_2(NO_3)_2]_2,$$

long, pale yellow needles, darkening at 130°, sintering at 145°, m. p. 150·5—151° (decomp.); *hydrochloride*,

$$CH_2(C_6H_4{\cdot}NMe_2Cl{\cdot}OH)_2,$$

colourless, glistening needles, turning brown at 150°, m. p. 165·5—166° (decomp.); *platinichloride*, *aurichloride*, and *hydrogen ferrocyanide* are described. On reduction, the hydrochloride yields tetramethyldiaminodiphenylmethane, and when iron is used, traces of tetramethyldiaminobenzhydrol and tetramethyldiaminobenzophenone appear to be formed. With nitrous acid, the hydrochloride gives 3 : 3′-dinitrotetramethyldiaminodiphenylmethane, and when the dioxide is treated with sulphur dioxide, *tetramethyldiaminodiphenylmethane*-3 : 3′-*disulphonic acid* is produced.

By treating the dioxide with acetic anhydride and sulphuric acid, the substance undergoes intramolecular change, partly into *tetramethyldiamino*-3 : 3′-*dihydroxydiphenylmethane*,

$$CH_2[C_6H_3(OH)\cdot NMe_2]_2,$$

colourless, hard, glassy prisms, m. p. 114·5—115°, and partly, with simultaneous formation of tetramethyldiaminodiphenylmethane, into *tetramethyldiamino-3-hydroxydiphenylmethane*, white, silky needles, m. p. 111—111·5°.

4 : 4′-*Tetramethyldiaminotriphenylmethane dioxide*,

$$CHPh(C_6H_4\cdot NMe_2O)_2.$$

crystallises with $2H_2O$ (analysis by Rudolf) or $4H_2O$ (analysis by Reber), forming white, glistening needles, m. p. 131·5—132·5°. Its properties resemble those of the diphenylmethane derivative. The anhydrous substance has m. p. 188—189° (decomp.). The *picrate*, $C_{35}H_{32}O_{16}N_8$, *platinichloride*, and *hydrogen ferrocyanide* are described. On reduction, the dioxide yields leuco-malachite-green, and, when iron is used, also probably some tetramethyldiaminotriphenylcarbinol.

By the action of nitrous acid, an orange-yellow, uncrystallisable powder is formed, which is probably 3 : 3′-*dinitrotetramethyldiaminotriphenylmethane*, $CHPh[C_6H_3(NO_2)\cdot NMe_2]_2$; on reduction, this yields 3: 3′-*diaminotetramethyldiaminotriphenylmethane*, pale brown, amorphous flakes; the *platinichloride*, $C_{23}H_{26}N_4,H_2PtCl_6$, was prepared. By the action of acetic anhydride and sulphuric acid, the dioxide is converted into 4 : 4′-*tetramethyldiamino*-3 : 3′-*dihydroxytriphenylmethane*, colourless needles, m. p. 183—184°.

4 : 4′ : 4″-*Hexamethyltriaminotriphenylmethane trioxide*,

$$CH(C_6H_4\cdot NMe_2O)_3,$$

forms hair-like, colourless needles, m. p. 176°; the *picrate*,

$$C_{43}H_{40}O_{24}N_{12},$$

and *platinichloride* are described. On reduction, it yields leuco-crystal-violet, and by the action of nitrous acid it gives 3 : 3′ : 3″-*trinitro*-4 : 4′ : 4″-*hexamethyltriaminotriphenylmethane*,

$$CH[C_6H_3(NO_2)\cdot NMe_2]_3,$$

orange-yellow flakes, which, on reduction, furnishes 3 : 3′ : 3″-*triamino*-4 : 4′ : 4″-*hexamethyltriaminotriphenylmethane*, white needles, m. p. 221·5—223·5°; the *platinichloride* is described.

By the action of acetic anhydride and sulphuric acid, the trioxide is converted into leuco-crystal-violet and 4 : 4′ : 4″-*hexamethyltriamino*-3 : 3′ : 3″-*trihydroxytriphenylmethane*, a pale bluish-green powder.

J. C. C.

Negative Substituted Amino-oximes. II. Phenylnitroethenylamino-oxime. Wilhelm Steinkopf and Czeslau Benedek (*Ber.*, 1908, 41, 3566—3568. Compare Steinkopf and Bohrmann, Abstr., 1907, i, 480; this vol., i, 327).—It has been shown previously that the ease with which the halogenated and nitro-substituted ethenylamino-oximes are formed, and their comparative stability towards water, results from the negative influence of the substituting groups. It was of interest, therefore, to study the influence of a phenyl-substituting group, which is negative like the halogens and nitro-group, but occupies a greater volume. It is now found that, whilst phenylnitroethenylamino-oxime is readily formed, it is unstable, and decomposes in a closed vessel in the course of a few days, or more slowly in an open vessel. Hydroxylamine can be detected in the cold aqueous solution of the amino-oxime.

Phenylnitroethenylamino-oxime, $NO_2\cdot CHPh\cdot C(NOH)\cdot NH_2$, prepared by the action of hydroxylamine hydrochloride on a concentrated aqueous solution of sodium *aci*-phenylnitroacetonitrile at the laboratory temperature, forms white crystals, m. p. 125°, reduces mercuric chloride in cold alkaline solution, gives a violet coloration with ferric chloride, and forms a *hydrochloride*, which separates in white crystals, m. p. 153°. The amino-oxime acts as a dibasic acid, forming two series of salts. The *copper*, $C_8H_7O_3N_3Cu$, and *barium*, $(C_8H_8O_3N_3)_2Ba$, salts were analysed. G. Y.

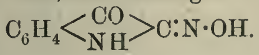
Indigotin Group. HEINRICH WIELAND and ERWIN GMELIN (*Ber.*, 1908, 41, 3512—3517. Compare Wieland and Semper, this vol., i, 108).—The ethyl glyoximeperoxidedicarboxylate discovered by Pröpper (*Annalen*, 1884, 222, 46) is converted by barium hydroxide into barium furoxandicarboxylate. This salt reacts with aniline hydrochloride, forming iso*nitrosomalonanilideoxime*,

$$CO_2H\cdot C(:N\cdot OH)\cdot C(:N\cdot OH)\cdot NHPh,$$

and this when warmed with acetic anhydride is converted into *cyano-N-acetylformanilideoxime*, $CN\cdot C(:N\cdot OH)\cdot NAcPh$. On warming with ammonium sulphide, *oxanilideoxime-thiamide*,

$$NH_2\cdot SC\cdot C(:N\cdot OH)\cdot NH\cdot C_6H_5,$$

is formed, which, on warming with concentrated sulphuric acid, gives α-isatoxime,



$$C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C:N\cdot OH.$$

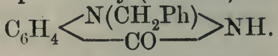
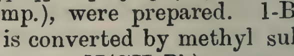
Ethyl furoxandicarboxylate is hydrolysed with baryta and heated at 30—40° with concentrated aqueous aniline hydrochloride. The *aniline* salt of *iso*nitrosomalonanilideoxime separates in yellow crystals, m. p. 133°; the corresponding acid obtained by hydrolysis with hydrogen chloride forms colourless plates, m. p. 165—166° (decomp.); it gives a blackish-green coloration with ferric chloride. The *barium* salt is light yellow; the *sodium hydrogen* salt, colourless. *Cyano*-N-*acetylformanilideoxime* crystallises in large, colourless prisms, m. p. 135°; it does not give a coloration with ferric chloride. *Oxanilideoxime-thiamide* forms bright yellow crystals, m. p. 169—171°, and shows the characteristic dark green ferric chloride reaction. It is added in portions to sulphuric acid, maintained at 60°, and the temperature is gradually raised until sulphur dioxide fumes are evolved, when the solution is poured on to ice, neutralised, and the α-isatoxime extracted with ethyl acetate. E. F. A.

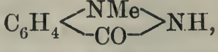
Hydrazones of Sugars. A. RECLAIRE (*Ber.*, 1908, 41, 3665—3671). —The *o*-, *m*-, and *p*-nitrophenylhydrazones of various sugars have been prepared in aqueous-alcoholic or in acetic acid solution. Many of them have already been described by Alberda van Ekenstein and

Blanksma (Abstr., 1904, i, 98). The following new compounds are mentioned: Dextrose forms a m-*nitrophenylhydrazone*, m. p. 115—116°, m-*nitrophenylosazone*, m. p. 228°, o-*nitrophenylhydrazone*, m. p. 148°, and o-*nitrophenylosazone*, m. p. 215—217°. Mannose forms a m-*nitrophenylhydrazone*, m. p. 162—163°, an impure m-*nitrophenylosazone*, m. p. 214° (decomp.), and an o-*nitrophenylhydrazone*, m. p. 173°. Lævulose forms an o-*nitrophenylhydrazone*, m. p. 155—156°. Galactose forms a m-*nitrophenylhydrazone*, m. p. 181—182°, and an o-*nitrophenylhydrazone*, m. p. 172. Arabinose forms a m- and an o-*nitrophenylhydrazone*, m. p. 179—180° and 180° respectively. Xylose forms a m-*nitrophenylhydrazone*, m. p. 130° (decomp. at 120°). Rhamnose forms a m- and an o-*nitrophenylhydrazone*, m. p. 104—105° and 151° respectively. C. S.

Action of Secondary *as*-Hydrazines on Carbamide. Hugo Milrath (*Monatsh.*, 1908, **29**, 909—935).—Most of the matter in this communication has already been abstracted (this vol., i, 581). Phenylbenzylsemicarbazide, when heated with acetic anhydride, yields *diacetyl*-as-*phenylbenzylhydrazine*, $C_{17}H_{18}O_2N_2$ m. p. 128° (compare Milrath, *loc. cit.*), which may also be prepared directly from *as*-phenylbenzylhydrazine.

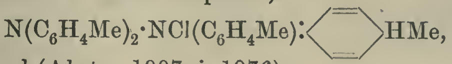
Diphenyldimethylsemicarbazide may be prepared by heating carbamide (1 mol.) with *as*-phenylmethylhydrazine (2 mols.) at 170—180°.

The substance, m. p. 167—168°, described previously (*loc. cit.*), is now shown to be 1-*benzylbenzopyrazolone*,  $C_6H_4<\substack{N(CH_2Ph)\\CO}>NH$. It may also be prepared by acting on benzopyrazolone (anhydro-*o*-hydrazinobenzoic acid: Fischer and Renouf, Abstr., 1882, 1068) with benzyl chloride and sodium methoxide. The white, crystalline *hydrochloride*, $C_{14}H_{12}ON_2,HCl$, yellow, crystalline *platinichloride*, m. p. 134—138° (decomp.), and *picrate*, $C_{14}H_{12}ON_2,C_6H_3O_7N_3$, large, dark yellow plates, m. p. 154—155° (decomp.), were prepared. 1-Benzylbenzopyrazolone in alkaline solution is converted by methyl sulphate into 1-*benzyl*-2-*methylbenzopyrazolone*,  $C_6H_4<\substack{N(CH_2Ph)\\CO}>NMe$, which crystallises with $1H_2O$ in long, slender, silky, white needles, softens at 65°, and has m. p. 75—80°.

1-*Methylbenzopyrazolone*,  $C_6H_4<\substack{NMe\\CO}>NH$, obtained by heating carbamide (1 mol.) with *as*-phenylmethylhydrazine at 170—180°, and finally at 270—280°, has m. p. 153—154°. W. H. G.

Decomposition of Tetra-arylhydrazines. IV. Heinrich Wieland (*Ber.*, 1908, **41**, 3478—3498. Compare Abstr., 1907, i, 1076).—Aromatic hydrazines are decomposed by various acid reagents in accordance with the equation: $Ar_2N\cdot NAr_2 + HR \longrightarrow Ar_2NH + RNAr_2$. Diarylamines and a molecule comprising the acid residue R result. In the case of hydrogen chloride, the hypothetical product will be a diarylamine containing chlorine attached to nitrogen, NAr_2Cl. Such secondary aromatic chloroamines are not known, and attempts to synthesise them have only yielded hydrazines, $Ar_2N\cdot NAr_2$, or compounds substituted in the nucleus. On decomposition of tetraphenylhydrazine, two molecules of chloroamine unite, with elimination of hydrogen chloride, in the para-position, $C_6H_5\cdot NCl\cdot C_6H_4\cdot NPh_2$. This primary product undergoes rearrangement to *p*-chloroanilinotriphenylamine, $Cl\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NPh_2$ (Gambarjan, following abstract).

In the case of tetra-*p*-tolylhydrazine, two molecules of the chloroamine unite in the ortho-position, two mols. of hydrogen chloride being eliminated, and a completely substituted phenazine ring compound is obtained. In addition, chlorinated phenazine compounds containing two halogen atoms in the nucleus are formed, due to the oxidising action of the chloroamine. The first product of the decomposition is the violet quinonoid additive compound,

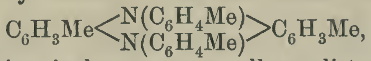


already described (Abstr., 1907, i, 1076).

Other acids act similarly to hydrogen chloride, and the primary products of the type $NAr_2\cdot OR$ are to be regarded as derivatives of the hypothetical diphenylhydroxylamine, $NPh_2\cdot OH$.

Tetra-anisylhydrazine is not obtained on oxidation of *p*-dianisylamine, but a ditertiary azine is formed by elimination of water from two molecules of the unstable hydroxylamine.

The ditertiary phenazine derivatives, conveniently termed "perazines," are stable towards oxidising agents. They form coloured salts with mineral acids, carboxylic acids, or phenols in anhydrous solvents, which are, as a rule, mono-acid, and are regarded as quaternary quinolimonium compounds. On oxidation, a series of salts of other colours are obtained, which possibly represent the *o*-quinonoidbisphenazonium series.

By the action of hydrogen chloride in ether on tetratolylhydrazine in chloroform solution, the violet solution of the quinolimonium salt is first obtained, which changes subsequently to red, and deposits glistening, dark green, flat needles of *dichloroditolyltolazonium hydrochloride*. Alkalis decompose this into *dichloroditolyldihydrotolazine*, which is obtained from xylene in lustrous, garnet-red, four-sided prisms. It is very stable, and begins to decompose above 360°. With bromine, it forms a dark violet additive product containing one mol. of bromine. By reduction with sodium and amyl alcohol, p-*ditolyldihydrotolazine*,  $C_6H_3Me{<}{\begin{matrix}N(C_6H_4Me)\\N(C_6H_4Me)\end{matrix}}{>}C_6H_3Me$, is quantitatively formed, crystallising in long, orange-yellow, glistening needles, m. p. 269°; it can be distilled without decomposition. Both ditolyldihydrotolazine and its dichloro-derivative are formed by the action of hydrogen chloride on tetratolylhydrazine, but the latter is the main product.

Ditolyldihydrotolazine itself does not exhibit the properties of a base, and can be heated with aqueous acids without forming salts. With alcoholic or ethereal acid solutions, it forms dark green azonium salts, of which the *hydrochloride* is particularly characteristic; it separates in dark green, glistening, broad needles. The normal salt contains one molecule of acid, but there is a tendency to form an acid salt. The *nitrate* forms minute, dark green needles, decomp. 236°. Decomposition of the salts with sodium hydroxide leads to the formation of basic by-products; alcoholic potassium hydroxide or zinc dust afford better means of effecting the decomposition.

Acetic acid acts very readily on tetratolylhydrazine; the solution becomes at first dark violet, owing to the formation of the quinonoid hydrazonium acetate, and then dark green, owing to conversion into tolazonium acetate. On adding water, *p*-ditolylamine separates, and ditolyldihydrotolazine may be obtained from the mother liquors.

Phosphoryl chloride or phosphorus trichloride and benzoyl chloride do not react with tetratolylhydrazine in the absence of water. When moisture is present, large, dark green crystals are obtained; their formation is due to the hydrogen chloride slowly liberated by the chlorides, which gives rise to dichlorotolazonium chloride and phosphate.

p-*Dianisylamine*, $(OMe\cdot C_6H_4)_2NH$, prepared by Goldberg's method (this vol., i, 17), does not yield tetra-anisylhydrazine on oxidation, but an *azine*, $C_{28}H_{26}O_4N_2$, crystallising in stellar aggregates of bright yellow needles, m. p. 290°. The *anisazonium* salts are similar to the tolylazonium compounds; the *hydrochloride* forms green, glistening needles; the *nitrate* is obtained as a wine-red precipitate, m. p. 223° (decomp.). The *ferrichloride* separates in bronze, glistening, violet-red plates; the *chromate* forms dark red needles; the *platinichloride* is insoluble in water, and likewise the *ferro-* and *ferri-cyanides*, of which the former yields a rose-red, the latter a brownish-red, precipitate.

Wool is quickly dyed by anisazonium salts in fast, scarlet-red shades. Anisazonium chloride is dissolved by pyridine without change, but gives an intense sea-blue coloration with aniline. Oxidising agents convert the anisazonium salts into green compounds, which are unstable, and pass slowly in solution into carmine substances. The new perazonium salts have characteristic absorption bands in their spectra. E. F. A.

Decomposition of Tetraphenylhydrazine with Hydrogen Chloride. STEFAN GAMBARJAN (*Ber.*, 1908, 41, 3507—3512).—In a previous paper (Wieland and Gambarjan, Abstr., 1906, i, 453) it was stated that tetraphenylhydrazine, when treated with hydrogen chloride in anhydrous ethereal solution, formed diphenylamine hydrochloride and *p*-chlorodiphenylamine. It is now found that the latter compound is not produced, but that a secondary base, p-*chloroanilinotriphenylamine*, is formed. The constitution of this has been established by elimination of the chlorine by means of sodium and the identification of the product with *anilinotriphenylamine* (triphenyl-*p*-phenylenediamine), prepared synthetically by treating diphenylamine with *p*-iodonitrobenzene, reducing the nitro-group, acetylating, and again treating with iodobenzene.

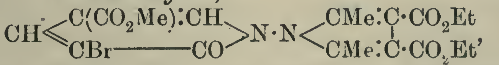
The decomposition of the tetraphenylhydrazine is quantitative. The dark green quinolimonium salt is first formed, and decomposes to colourless diphenylamine and diphenylchloroamine. Two molecules of the latter then interact, and chlorine is eliminated.

p-*Chloroanilinotriphenylamine*, $NPh_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4Cl$, has b. p. 205—215°/0·01 mm., m. p. 77—81°, and forms a crystalline *hydrochloride* and an *acetyl* derivative, m. p. 199—200°. p-*Anilinotriphenylamine*, prepared from this by means of sodium, has m. p. 134°, and yields an *acetyl* derivative, m. p. 184°.

p-*Nitrotriphenylamine* crystallises in rectangular plates, m. p. 144°, insoluble in acetic acid. p-*Aminotriphenylamine* has m. p. 145—148°, and forms an *acetyl* derivative, crystallising in silvery plates, m. p. 195°. E. F. A.

Action of *N*-Amino-compounds on Bromocoumalinic Acid Esters. Carl Bülow and Hans Filchner (*Ber.*, 1908, **41**, 3281—3285).—Compounds containing two similar ring systems united by the $>N \cdot N<$ group have been described by Bülow and Sautermeister (Abstr., 1904, i, 690) and by von Pechmann and Mills (Abstr., 1904, i, 1042). Bülow (Abstr., 1906, i, 905; 1907, i, 99) has also prepared a compound containing two different five-membered rings united by the same grouping. The authors have not succeeded in preparing a compound containing a five-membered and a six-membered ring joined together by the group $>N \cdot N<$.

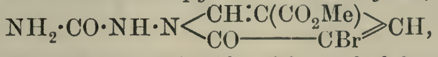
5-*Methyl* 3′ : 4′-*diethyl* 1′-(3-*bromo*-5-*carboxy*-2-*pyridonyl*)-2′ : 5′-*dimethylpyrrole*-3′ : 4′-*dicarboxylate*,



$$\mathrm{CH}\lessgtr\begin{matrix}\mathrm{C(CO_2Me){:}CH}\\ \mathrm{CBr{-}{-}{-}{-}CO}\end{matrix}>\mathrm{N\cdot N}<\begin{matrix}\mathrm{CMe{:}C\cdot CO_2Et}\\ \mathrm{CMe{:}C\cdot CO_2Et}\end{matrix},$$

prepared by condensing methyl bromocoumalinate with ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate in presence of glacial acetic acid, forms colourless needles, m. p. 155°.

Methyl 3-*bromo*-1-*carbamido*-2-*pyridone*-5-*carboxylate*,



$$\mathrm{NH_2\cdot CO\cdot NH\cdot N}<\begin{matrix}\mathrm{CH{:}C(CO_2Me)}\\ \mathrm{CO{-}{-}{-}{-}CBr}\end{matrix}\gtrless\mathrm{CH},$$

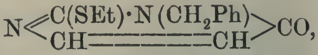
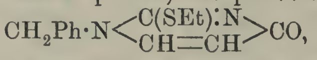
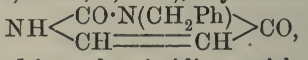
prepared by condensing semicarbazide with methyl bromocoumalinate, forms colourless needles, m. p. 223°. On hydrolysis, it yields 3-*bromo*-1-*carbamido*-2-*pyridone*-5-*carboxylic acid*, m. p. 252°. J. C. C.

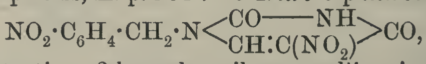
Preparation of 5 : 5-Dialkylbarbituric Acids. Chemische Fabrik auf Actien (vorm. E. Schering) (D.R.-P. 201244).—Dimethyl- and diethyl-malonylguanidines, when hydrolysed with boiling 10% sulphuric acid, or at 120° with concentrated hydrochloric or hydrobromic acid, give rise to the corresponding 5 : 5-dialkylbarbituric acids. G. T. M.

4 : 6-Dihydroxy-2-phenylpyrimidine. E. L. Pinner (*Ber.*, 1908, **41**, 3517—3519).—4 : 6-*Dihydroxy*-2-*phenylpyrimidine*, $C_{10}H_8O_2N_2$, prepared by the interaction of equivalent quantities of benzamidine hydrochloride and ethyl malonate in the presence of sodium ethoxide at the ordinary temperature, forms crystals, m. p. 325—330°. It is converted by bromine in glacial acetic acid into 5-*bromo*-4 : 6-*dihydroxy*-2-*phenylpyrimidine*, $C_{10}H_7O_2N_2Br$, crystallising in pale yellow needles, m. p. 320° (decomp.), and by acetic anhydride into a *monoacetate*,

$C_{12}H_{10}O_3N_2$, glistening, flat prisms, m. p. 195°, and a *diacetate*, $C_{14}H_{12}O_4N_2$, brilliant, flat prisms, m. p. 93—94°. 4-*Hydroxy*-6-*ethoxy*-2-*phenylpyrimidine*, $C_{12}H_{12}O_2N_2$, is formed by heating the dihydroxy-compound with ethyl bromide and an alcoholic solution of potassium hydroxide under pressure at 100°; it crystallises in flat prisms, m. p. 174°. W. H. G.

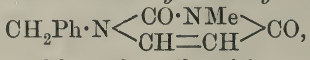
Pyrimidines. XXXVIII. Syntheses of some Benzyl Derivatives of Uracil and Thymine. TREAT B. JOHNSON and JOHN H. DERBY, jun. (*Amer. Chem. J.*, 1908, **40**, 444—458).—The authors have synthesised 1- and 3-benzyluracil and 1- and 3-benzylthymine.

2-*Ethylthiol*-6-*oxy*-1-*benzylpyrimidine*,  $N{<}\begin{matrix}C(SEt)\cdot N(CH_2Ph)\\ CH=\!=\!=\!=\!=\!=CH\end{matrix}{>}CO$, prepared by the action of benzyl chloride on 2-ethylthiol-6-oxypyrimidine, forms prisms, m. p. 77°. 2-*Ethylthiol*-6-*oxy*-3-*benzylpyrimidine*,  $CH_2Ph\cdot N{<}\begin{matrix}C(SEt){:}N\\ CH=CH\end{matrix}{>}CO$, formed by the same reaction and isolated through its insolubility in ether, crystallises in long, slender prisms and hexagonal prisms or flat tablets, m. p. 139°. 5-*Bromo*-2-*ethylthiol*-6-*oxy*-3-*benzylpyrimidine*, prepared by the interaction of benzyl chloride and 5-bromo-2-ethylthiol-6-oxypyrimidine (Wheeler and Johnson, Abstr., 1904, i, 624), crystallises in needles, m. p. 129°. 1-*Benzyluracil*,  $NH{<}\begin{matrix}CO\cdot N(CH_2Ph)\\ CH=\!=\!=\!=CH\end{matrix}{>}CO$, prepared by evaporating 2-ethylthiol-6-oxy-1-benzylpyrimidine with hydrochloric acid, forms prismatic crystals, m. p. 175°. It gives a red colour with diazobenzenesulphonic acid. 3-*Benzyluracil*, prepared similarly from 2-ethylthiol-6-oxy-3-benzylpyrimidine, crystallises in stout prisms, m. p. 173°. It gives only a yellow colour with diazobenzenesulphonic acid (distinction from 1-benzyluracil). 5-*Bromo*-3-*benzyluracil*, prepared by brominating 3-benzyluracil or by digesting 5-bromo-2-ethylthiol-6-oxy-3-benzylpyrimidine with concentrated hydrochloric acid, forms hexagonal prisms, m. p. 204°. 5-*Nitro*-3-p-*nitrobenzyluracil*,

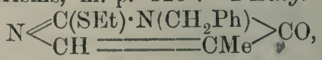


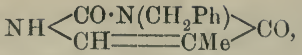
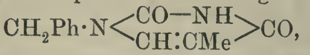
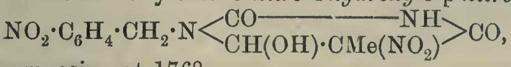
$$NO_2\cdot C_6H_4\cdot CH_2\cdot N{<}\begin{matrix}CO\text{——}NH\\ CH{:}C(NO_2)\end{matrix}{>}CO,$$

prepared by nitrating 3-benzyluracil, crystallises in slender prisms, decomposing at 235—240°. 3-*Benzyl*-1-*methyluracil*,



$$CH_2Ph\cdot N{<}\begin{matrix}CO\cdot NMe\\ CH=CH\end{matrix}{>}CO,$$

prepared by treating 3-benzyluracil with methyl iodide or from 1-methyluracil and benzyl chloride, forms needles, m. p. 75°. On bromination, it gives 5-*bromo*-3-*benzyl*-1-*methyluracil*, which is also formed by the interaction of methyl iodide and 5-bromo-3-benzyluracil; it crystallises in diamond-shaped prisms, m. p. 123°. 2-*Ethylthiol*-6-*oxy*-1-*benzyl*-5-*methylpyrimidine*,  $N{<}\begin{matrix}C(SEt)\cdot N(CH_2Ph)\\ CH=\!=\!=\!=\!=CMe\end{matrix}{>}CO$, prepared by the interaction of benzyl chloride and 2-ethylthiol-6-oxy-5-methylpyrimidine, forms stout prisms, m. p. 70°; in the same reaction there is also formed (insoluble in ether) 2-*ethylthiol*-6-*oxy*-3-*benzyl*-5-*methylpyrimidine*, crystallising in hexagonal plates, m. p.

121—122°. 1-*Benzylthymine*,  $NH<\begin{smallmatrix}CO\cdot N(CH_2Ph)\\ CH=\!=\!=\!=CMe\end{smallmatrix}>CO$, prepared by digesting 2-ethylthiol-6-oxy-1-benzyl-5-methylpyrimidine with concentrated hydrochloric acid, forms clusters of radiating prisms, m. p. 204—205°; with diazobenzenesulphonic acid it gives a claret-red solution. 3-*Benzylthymine*,  $CH_2Ph\cdot N<\begin{smallmatrix}CO-NH\\ CH{:}CMe\end{smallmatrix}>CO$, similarly prepared from 2-ethylthiol-6-oxy-3-benzyl-5-methylpyrimidine, forms diamond-shaped prisms, m. p. 160°. It gives only a yellow colour with diazobenzenesulphonic acid. 3-*Benzyl*-1-*methylthymine*, obtained by the action of methyl iodide on 3-benzylthymine, forms prismatic crystals, m. p. 101°; it does not react with diazobenzenesulphonic acid. On nitration it yields 5-*nitro*-4-*hydroxy*-3-p-*nitrobenzyldihydrothymine*,  $NO_2\cdot C_6H_4\cdot CH_2\cdot N<\begin{smallmatrix}CO-\!-\!-\!-\!-\!-NH\\ CH(OH)\cdot CMe(NO_2)\end{smallmatrix}>CO$, which forms prisms decomposing at 176°. J. C. C.

Preparation of 4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. Emil Scheittin (D.R.-P. 199844).—4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone is readily obtained in good yield by heating 4-sulphonylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone with methyl sulphate in alcoholic solution at 100—115° (compare this vol., i, 688). G. T. M.

Preparation of Chlorobromoindigotin. Gesellschaft für Chemische Industrie in Basel (D.R.-P. 198816. Compare this vol., i, 695).—*Chlorobromoindigotin*, obtained by heating at 226° in nitrobenzene, chloroindigotin (1 mol.) and bromine (1 mol.), is a blue, crystalline powder, sparingly soluble in water, alcohol, or benzene, but dissolving more readily in warm aniline or nitrobenzene.

On reduction with alkaline reducing agents, it furnishes a light yellow leuco-derivative. G. T. M.

Halogen Indigotins. Carl G. Schwalbe and Hermann Jochheim (*Ber.*, 1908, **41**, 3796—3798).—A table is given of the colours of *o*-, *m*-, and *p*-dichloroindigotin and indigotin in sulphuric acid, alcohol, chloroform, acetic acid, pyridine, aniline, and nitrobenzene solutions, together with observations on the preparation of the three chloro-*o*-nitrobenzaldehydes; Müller's fourth isomeride is a mixture of *m*-chloro-*o*-nitrobenzaldehyde and unchanged aldehyde. W. R.

Halogen Indigotinsulphonic Acids. Carl G. Schwalbe and Hermann Jochheim (*Ber.*, 1908, **41**, 3798—3802).—A halogen phenylglycine mixed with sand, when washed with excess of cold sulphuric acid (60% SO_3), yields a halogen indigotinsulphonic acid; the purification is carried out by extraction with amyl alcohol and fractional precipitation with petroleum or benzene, the usual methods not giving satisfactory results. *m*-Chlorophenylglycine gives a dichlorotetrasulphonic acid; the *p*-chloro-derivative, a dichlorohexasulphonic acid, and the 2 : 4-dichloro-compound, a tetrachlorodisulphonic acid; *o*-chlorophenylglycine does not form a dye; the *o*-bromo-compound gives a dye which does not contain halogen. A comparison of the aqueous solutions of these sulphonic acids and indigo-carmine as regards colour and dyeing properties is given. W. R.

Constitution of the Acid Derivatives of Methylhydrazine. August Michaelis and Erich Hadanck (*Ber.*, 1908, **41**, 3285—3290). —In attempting to prepare 5-phenyl-1-methyl-3-pyrazolone by the action of phosphorus trichloride on a mixture of ethyl benzoylacetate and an acid derivative of methylhydrazine, the authors invariably obtained 3-phenyl-1-methyl-5-pyrazolone, which is also produced by the condensation of methylhydrazine and ethyl benzoylacetate. As 3-pyrazolones are so often obtained by Michaelis and Mayer's reaction, the above fact could only be explained by the migration of the methyl group from the one nitrogen atom to the other, or else by the more probable assumption that the acid derivatives of methylhydrazine employed have an unsymmetrical constitution. The authors find that methylsemicarbazide, methylthiosemicarbazide, and mono- and dibenzoylmethylhydrazines have an unsymmetrical constitution, as they condense readily with aldehydes with the formation of hydrazones, whilst oxalyldimethylhydrazine appears to be symmetrically constituted.

Benzylidenemethylsemicarbazide, $NH_2\cdot CO\cdot NMe\cdot N:CHPh$, prepared by the action of benzaldehyde on methylsemicarbazide, forms white needles, m. p. 162°. p-*Methoxybenzylidenemethylsemicarbazide*,

$$NH_2\cdot CO\cdot NMe\cdot N:CH\cdot C_6H_4\cdot OMe,$$

similarly prepared from anisaldehyde, forms silky needles, m. p. 191°. The constitution of methylsemicarbazide is therefore

$$NH_2\cdot CO\cdot NMe\cdot NH_2,$$

and, in accordance with this, it reacts with carbon disulphide to form *bis-methylcarbamidothiocarbamide*, $CS(NH\cdot NMe\cdot CO\cdot NH_2)_2$, white needles, m. p. 253·5°. When methylhydrazine is treated with carbon disulphide, there is formed the *salt*, $NHMe\cdot NH\cdot CS\cdot S\cdot NH_3\cdot NHMe$, which loses hydrogen sulphide and yields *bis-methylaminothiocarbamide*, $CS(NH\cdot NHMe)_2$, white needles, m. p. 241°.

Phenylbenzylidenemethylthiosemicarbazide, $NHPh\cdot CS\cdot NMe\cdot N:CHPh$, prepared by the interaction of benzaldehyde and phenylmethylthiosemicarbazide, forms long, glistening needles, m. p. 131·5°.

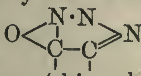
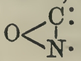
Benzoylbenzylidenemethylhydrazine, $NMeBz\cdot N:CHPh$, prepared by the interaction of benzaldehyde and crude *monobenzoylmethylhydrazine* (an oil from benzoic anhydride and methylhydrazine), forms small, white needles, m. p. 82°.

Benzoylanisylidenemethylhydrazine, $NMeBz\cdot N:CH\cdot C_6H_4\cdot OMe$, prepared from anisaldehyde, forms slender, white needles, m. p. 115°. When benzoylmethylhydrazine in alcoholic or ethereal solution is shaken with yellow mercuric oxide, an oil is obtained which has the properties of a tetrazone; this could not, however, be prepared in the pure state.

Dibenzoylmethylhydrazine can be prepared by treating methylhydrazine with benzoic anhydride; it has m. p. 145° (von Brüning, Abstr., 1890, 23, gives 143°).

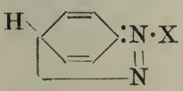
Diacetylmethylhydrazine, NMeAc·NHAc, is a colourless oil, b. p. 280°.

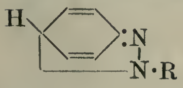
Oxalyldimethylhydrazine does not yield a hydrazone with either benzaldehyde or anisaldehyde. J. C. C.

Constitution of the Endoxypyrrodiazoles [4 : 5-Oxy-1 : 2 : 5-osotriazoles]. GIACOMO PONZIO (*Gazzetta*, 1908, **38**, ii, 522—524. Compare Abstr., 1898, i, 386; 1899, i, 717, 827; 1900, i, 588; 1901, i, 169; 1902, i, 190).—The author's conclusion, that the compounds obtained by the oxidation of the hydrazoximes (*loc. cit.*) contain the nucleus  $O<\overset{N\cdot N}{\underset{C-C}{|}}>N$, is confirmed by the recent work of Wieland and Semper (this vol., i, 108), who find that phosphorus pentachloride does not react with compounds containing the group $:N:O$, whilst it readily transforms compounds containing the complex  $O<\overset{C:}{\underset{N\cdot}{|}}$ into the corresponding compounds containing the grouping $:C:N\cdot$.

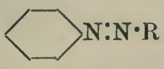
The interaction of phosphorus pentachloride and 4 : 5-oxy-1-phenyl-3 : 4-dimethyl-1 : 2 : 5-osotriazole yields 1-phenyl-3 : 4-dimethyl-1 : 2 : 5-osotriazole, which partly undergoes chlorination to 1-*p*-chlorophenyl-3 : 4-dimethyl-1 : 2 : 5-osotriazole. T. H. P.

Cain's Theory of Diazo-compounds and Ammonium Salts. ARTHUR HANTZSCH (*Ber.*, 1908, **41**, 3532—3536).—A criticism of Cain's theory of diazo-compounds (compare Trans., 1907, **91**, 1049) and of ammonium salts. The main objections raised by the author are briefly as follows: (1) diazobenzene salts have the properties of true benzene derivatives, and not those of derivatives of dihydrobenzene, as represented by the annexed formula; (2) the behaviour of diazo-salts when reduced or oxidised, or when treated with halogen, is not in agreement with the presence of an unsaturated ring, as shown by this formula; (3) a compound having such a constitution, when reduced, should yield *p*-phenylenediamine; (4) since both normal and *iso*diazo-compounds are very similar in their chemical behaviour, they cannot be represented by formulæ so different as those annexed. The fact that the isomeric diazocyanides give similar absorption spectra (compare Dobbie and Tinkler, Trans., 1905, **87**, 273) shows that these compounds must have very similar constitutions; (5) if tetraethylammonium chloride has the formula $NEt_3:Cl\cdot Et$, and undergoes ionisation in aqueous solution, thus: $NEt_3:Cl\cdot Et \longrightarrow NEt_3 + Et\cdot Cl \longrightarrow NEt_4^{\cdot} + Cl'$, it should be possible to detect the triethylamine and ethyl chloride produced as intermediate products, since these compounds interact but very slowly at low temperatures. As the formation of these compounds cannot be detected, the above supposition is untenable. W. H. G.





and



Decomposition of Diazo-solutions. ARTHUR HANTZSCH and KENWORTHY J. THOMPSON (*Ber.*, 1908, **41**, 3519—2532).—An investigation on the rates of decomposition of aqueous solutions of various diazo-salts, carried out with the object of clearing up several points which were still unsettled (compare Schwalbe, Abstr., 1905, i, 618; Cain, *ibid.*, i, 724).

Freshly prepared diazobenzene chloride contains traces of a substance, the nature of which could not be determined, which acts as a preservative. It disappears when the diazo-compound is kept for some time in a desiccator, or when a current of dry air is passed over the substance; consequently, solutions of the freshly prepared salt are more stable ($k = 0{\cdot}0008 - 0{\cdot}0009$) than those of the substance which has been kept for some days, or treated with a current of dry air, when the maximum value of k found was 0·00118 (compare Hantzsch and Osswald, Abstr., 1900, i, 703; Euler, Abstr., 1903, i, 298). It is therefore evident that the keeping qualities of aqueous solutions of diazo salts may be greatly influenced by very slight traces of unknown impurities. Diazobenzene bromide in dilute solutions decomposes at about the same rate as the chloride. The velocity of decomposition increases slowly with the concentration, the increase in the case of the bromide being slightly greater than that of the chloride, probably because the undissociated bromide is less stable than the undissociated chloride. Further, the velocity of decomposition increases with the decomposition of the salt; this is probably due to the formation of a halogenated benzene, produced by the action of the hydrogen halide which is liberated. Diazobenzene iodide, even in very dilute solutions, decomposes far more rapidly than the chloride or bromide, probably because the chief reaction which takes place in this case, namely, the formation of iodobenzene, proceeds at a greater rate than the production of phenol. A velocity constant could not be obtained, owing to the complexity of the many reactions which take place during the decomposition of solutions of diazonium iodides.

The rate of decomposition of *p*-nitrodiazobenzene chloride increases with the concentration; since it is greatly accelerated by light, the solutions were kept as far as possible in the dark, the value obtained being $k = 0{\cdot}00020$ at 50° ($v = 9$). Neither hydrochloric acid nor acetic acid influences the rate of decomposition of solutions of pure *p*-nitrodiazobenzene chloride to any marked degree (compare Schwalbe, *loc. cit.*).

Diazo-acetates in aqueous solution do not decompose in a normal manner; the weaker the diazo-base the more abnormal is the course of the reaction. As was stated by Schwalbe, the presence of sodium chloride increases the stability of solutions of *p*-nitrodiazobenzene acetate.

Solutions of diazo-salts are slowly decomposed by nitrous acid (compare Cain, *loc. cit.*); the nitrous acid does not act as a catalyst, as stated by Schwalbe, but slowly disappears, since it is directly concerned in the decomposition. W. H. G.

[Preparation of Disazo-derivatives of 2-Amino-*p*-cresol.] Anilinfarben & Extract Fabriken vorm. J. R. Geigy (D.R.-P. 201377).—*2-Amino-p-tolyl toluene-p-sulphonate*, $C_7H_7{\cdot}SO_2{\cdot}O{\cdot}C_7H_6{\cdot}NH_2$, lustrous prisms, m. p. 78°, is obtained by reducing 2-nitro-*p*-tolyl toluene-*p*-sulphonate; it couples with diazonium salts and diazoarylsulphonic acids, yielding diazotisable *p*-aminoazo-derivatives, such as *sodium sulphobenzene-5-azo-2-amino-*p*-tolyl toluene-*p*-sulphonate*,

$$SO_3Na\cdot C_6H_4\cdot N_2\cdot C_7H_5(NH_2)\cdot O\cdot SO_2\cdot C_7H_7.$$

The diazo-compounds of these *p*-aminoazo-derivatives couple with naphthol in alkaline solution, and the resulting disazo-derivatives give valuable colouring matters on removing the toluene-*p*-sulphonic group by hydrolysis. G. T. M.

Azo-derivatives of 2-Chloro-*p*-anisidine- and 2-Chloro-*p*-phenetidine-sulphonic Acids. ACTIEN-GESELLSCHAFT FÜR ANILINFABRIKEN (D.R.-P. 189469).—Insoluble coloured salts of the azo-compounds, $NaSO_3\cdot C_6H_2Cl(OMe)\cdot N_2\cdot C_{10}H_6\cdot OH$ and

$$NaSO_3\cdot C_6H_2Cl(OEt)\cdot N_2\cdot C_{10}H_6\cdot OH,$$

are produced by double decomposition with barium or other metallic chlorides. When mixed with aluminium hydroxide, these substances give rise to scarlet lakes of great brilliancy and fastness. G. T. M.

Azo-derivatives of Phenol and of the Phenolcarboxylic Acids. EUGÈNE GRANDMOUGIN and HANS FREIMANN (*J. pr. Chem.*, 1908, [ii], 78, 384—408).—A continuation and extension of former work (compare Abstr., 1907, i, 664, 986, 987; this vol., i, 926).

Azo-derivatives of Phenols.—The *benzenesulphonyl* ester of *p*-hydroxyazobenzene crystallises in yellow needles, m. p. 109°. The *acetyl* derivative of bis-benzeneazophenol has m. p. 116°, and the *benzenesulphonyl* ester forms yellowish-brown needles, m. p. 99°. The *benzenesulphonyl* ester of tris-benzeneazophenol forms red crystals, m. p. 202°.

o-Tolueneazophenol has m. p. 107—108° (Noelting and Werner, Abstr., 1891, 212, give 102—103°; Paganini, Abstr., 1891, 556, gives 101°); the *acetyl* derivative crystallises in reddish-yellow leaflets, m. p. 68°, and the *benzenesulphonyl* ester forms small, orange leaflets, m. p. 64°. Bis-*o*-tolueneazophenol has m. p. 116° (Noelting and Werner, *loc. cit.*, give 146°; Paganini, *loc. cit.*, gives 116°). The *acetyl* derivative forms reddish-yellow needles, m. p. 75—76°. When bis-*o*-tolueneazophenol is prepared from diazotised *o*-toluidine and ethyl *p*-hydroxybenzoate, it has m. p. 150°, and the acetyl derivative has m. p. 98°. The nature of this difference is not yet known.

*Bis-*m*-tolueneazophenol* forms yellowish-brown needles, m. p. 94°; the *acetyl* derivative crystallises in yellow needles, m. p. 75°. *Tris-*m*-tolueneazophenol*, prepared by the action of *m*-diazotoluene on salicylic acid, forms brown needles, m. p. 160°. The *acetyl* derivative of *p*-tolueneazophenol has m. p. 95°; the *benzenesulphonyl* ester forms brownish-yellow leaflets, m. p. 114°. Bis-*p*-tolueneazophenol has m. p. 176°, and the acetyl derivative has m. p. 138° (Goldschmidt and Pollak, Abstr., 1892, 974, give 170° and 128° respectively). *Tris-*p*-tolueneazophenol* forms brownish-red needles, m. p. 238°; the *acetyl* derivative crystallises in golden needles, m. p. 187°. *2-*p*-Nitrobenzeneazo-4-benzeneazophenol*, prepared by treating *p*-hydroxyazobenzene with diazotised *p*-nitroaniline, has m. p. 196°; the *acetyl* derivative has m. p. 189°. 4-p-*Nitrobenzeneazo-2-benzeneazophenol*, prepared from *o*-hydroxyazobenzene and diazotised *p*-nitroaniline, has m. p. 189°; the *acetyl* derivative has m. p. 154°. 4-*Acetylamino*-2-p-*nitrobenzeneazophenol*, prepared by the interaction of *p*-nitrodiazobenzene and *p*-acetylaminophenol, forms brown needles, m. p. 227°; it is hydrolysed by 60% sulphuric acid to 4-*amino*-2-p-*nitrobenzeneazophenol*, golden crystals, m. p. 211°. *β-Naphthaleneazophenol* forms bronze needles, m. p. 240°; the *acetyl* derivative crystallises in brown needles, m. p. 180°.

Azo-derivatives of Salicylic Acid.—Methyl p-*nitrobenzeneazosalicylate* forms silky, orange needles, m. p. 166°; the *acetyl* derivative forms orange-yellow needles, m. p. 131°. The *acetyl* derivative of phenyl benzeneazosalicylate (Limpricht, Abstr., 1891, 1036) forms golden needles, m. p. 132°. Limpricht's phenyl bis-benzeneazosalicylate is hydroxyazobenzene. *Phenyl* p-*nitrobenzeneazosalicylate* crystallises in yellow needles, m. p. 165°; the *acetyl* derivative forms yellow needles, m. p. 155°. o-*Nitrobenzeneazosalicylaldehyde* forms brown crystals, m. p. 141°; the *phenylhydrazone* forms brown needles, m. p. 192°. *Methyl bis-benzeneazosalicylate* forms brown crystals, m. p. 141°; the *acetyl* derivative forms yellowish-red needles, m. p. 145°. *Methyl bis*-o-*tolueneazosalicylate* forms brownish-yellow needles, m. p. 154°. *Bis*-m-*tolueneazosalicylic acid* forms brownish-olive needles, m. p. 210°; the *acetyl* derivative forms yellow needles, m. p. 170°. *Bis*-p-*tolueneazosalicylic acid* crystallises in brown, felted needles, m. p. 214°; the *acetyl* derivative forms reddish-brown tablets, m. p. 198°. These bisazo-derivatives of salicylic acid are all prepared in alkali hydroxide solution.

Azo-derivatives of p-*Hydroxybenzoic Acid.*—The acetyl derivative of benzeneazo-*p*-hydroxybenzoic acid has m. p. 205°, not 198—199° as previously given. o-*Tolueneazo*-p-*hydroxybenzoic acid* crystallises in orange-yellow needles, m. p. 223°. In the preparation of this substance from diazotoluene chloride and *p*-hydroxybenzoic acid in alkali hydroxide solution, there are also formed bis-*o*-tolueneazophenol and *o*-tolueneazoindazole; the *acetyl* derivative of the latter forms golden-yellow needles, m. p. 163°, and the *benzoyl* derivative, yellow needles, m. p. 179.5°. p-*Tolueneazo*-p-*hydroxybenzoic acid* forms yellow needles, m. p. 236°; the *acetyl* derivative forms yellow needles, m. p. 205°.

Ethyl benzeneazo-*p*-hydroxybenzoate (Auwers and Röhrig, Abstr., 1897, i, 341) is readily prepared by the action of diazobenzene chloride on ethyl *p*-hydroxybenzoate; the *acetyl* derivative forms yellowish-orange needles, m. p. 137°. *Ethyl* o-*tolueneazo*-p-*hydroxybenzoate* has m. p. 105°.

Azo-derivatives of m-*Hydroxybenzoic Acid.*—Benzeneazo-*m*-hydroxybenzoic acid has m. p. 221° (Limpricht, *loc. cit.*, gives 213°); the *methyl* ester forms brown needles, m. p. 78—79°. *Bis-benzeneazo*-m-*hydroxybenzoic acid* occurs in two isomeric forms, namely, the 2:6- and the 4:6-bis-benzeneazo-derivatives. Of these, the α-acid (not specified) forms brown needles, m. p. 222—223°, and the *β*-acid has m. p. 226—227°; it is sparingly soluble in methyl alcohol, whilst the α-acid is readily soluble in this solvent. The *methyl* ester of the β-acid forms bronze-yellow, felted needles, m. p. 183°. J. C. C.

Azobenzene-*p*-hydrazinesulphonic Acid resulting from the Action of Sulphur Dioxide on Diazobenzene Sulphate and its Condensation with Aldehydes and Ketones. Julius Tröger and O. Müller (*J. pr. Chem.*, 1908, [ii], 78, 369—383).—In continuation of previous work (Tröger, Berlin, and Franke, Abstr., 1906, i, 994), the authors have prepared a further number of hydrazones by condensing azobenzene-*p*-hydrazinesulphonic acid with aldehydes and ketones in the presence of glacial acetic acid or alcoholic hydrochloric acid.

Benzeneazo-p-*tolylidene*-p-*hydrazone*,

$$C_6H_5\cdot N_2\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4Me,$$

prepared from *p*-tolualdehyde, crystallises in orange-yellow needles, m. p. 178°; the *hydrochloride* forms small, blue needles. *Benzeneazo-cuminylidene*-p-*hydrazone*, $C_6H_5\cdot N_2\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot C_3H_7$, prepared from cuminaldehyde, forms yellowish-red needles, m. p. 144—145°; the *hydrochloride* is dark blue. *Benzeneazo*-m-*chlorobenzylidene*-p-*hydrazone*, $C_6H_5\cdot N_2\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4Cl$, prepared from *m*-chlorobenzaldehyde, forms small, glistening, golden-yellow leaflets, m. p. 160·5°; the *sulphate* forms dark blue needles. *Benzeneazo*-m-*bromobenzylidene*-p-*hydrazone* crystallises in small, glistening, golden-yellow leaflets, m. p. 173°; the *sulphate* is blue. *Benzeneazo*-p-*aminobenzylidene*-p-*hydrazone*, prepared from *p*-aminobenzaldehyde, forms small, reddish-brown leaflets, darkening at 136°, and decomposing above this, the residue being completely melted at 180·5°. *Benzeneazo*-p-*dimethylaminobenzylidene*-p-*hydrazone* crystallises in cinnabar-red needles, m. p. 185·5°; the *hydrochloride* forms small, glistening, blue needles. *Benzeneazo*-p-*hydroxybenzylidene*-p-*hydrazone* forms dark red needles, m. p. 196°; the *hydrochloride* consists of dark blue needles. *Benzeneazofurfurylidene*-p-*hydrazone*,

$$C_6H_5\cdot N_2\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_4H_3O,$$

prepared from furfuraldehyde, forms reddish-brown tablets, m. p. 133°; the *hydrochloride* is brownish-black.

Benzeneazobenzophenone-p-*hydrazone*, $C_6H_5\cdot N_2\cdot C_6H_4\cdot NH\cdot N\colon CPh_2$, prepared from benzophenone, forms brownish-red leaflets, m. p. 144°; the *hydrochloride* forms blue needles or plates. *Benzeneazobenzil*-p-*hydrazone*,

$$C_6H_5\cdot N_2\cdot C_6H_4\cdot NH\cdot N\colon CPh\cdot CPh\colon N\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_5,$$

prepared from benzil, forms orange-red needles, m. p. 184—185°; the *hydrochloride* is blue. *Benzeneazobenzylidene*-p-*hydrazone hydrochloride* is a black powder. J. C. C.

Trisbenzeneazophenol. Léo Vignon (*Bull. Soc. chim.*, 1908, [iv], 3, 1030—1031).—In previous work (Abstr., 1904, i, 699) on bisbenzeneazophenol, the author obtained indications of the formation of a substance richer in nitrogen, and this has led him to repeat Grandmougin and Freimann's work on trisbenzeneazophenol (Abstr., 1907, i, 664). He confirms their results, but points out that the yield of the trisazo-substance is only 1% of the theoretical.

T. A. H.

Aromatic Tetrazens. V. HEINRICH WIELAND (*Ber.*, 1908, **41**, 3498—3506).—The tetrazens are decomposed by hydrogen chloride in a similar manner to the tetra-arylhydrazines:

$$NAr_2\cdot N\colon N\cdot NAr_2 = NHAr_2 + NAr_2Cl + N_2.$$

Thus tetratolyltetrazen yields first a quinonoid salt,

$$NAr_2\cdot N\colon N\cdot NClAr\colon C_6H_4MeH,$$

indicated by a violet coloration in solution, which is decomposed with evolution of nitrogen, and finally *p*-ditolylamine, tolazonium and dichlorotolazonium chloride result. Tetra-anisyltetrazen behaves similarly; acetic acid brings about this decomposition in the cold with remarkable ease.

p-*Tetratolyltetrazen*, $N(C_7H_7)_2\cdot N\colon N\cdot N(C_7H_7)_2$, prepared by oxidation of *p*-ditolylhydrazine, preferably with permanganate, crystallises in glistening, yellow needles, decomp. 134°. It is decomposed by hydrogen chloride or acetic acid to tolazine derivatives. With bromine, a bluish-violet coloration indicates a primary additive product, which changes to a brownish-green; but little ditolylamine along with much dibromotolazine is formed.

To prepare *p*-dianisylhydrazine, *p*-dianisylamine is converted into the *nitrosoamine*, crystallising in flat, bright yellow needles, m. p. 79°, and dissolving in concentrated sulphuric acid with a greenish-blue coloration. On reduction with zinc dust and acetic acid, the *dianisylhydrazine*, $NH_2\cdot N(C_6H_4\cdot OMe)_2$, is obtained in mother-of-pearl-like, broad pointed, colourless needles, m. p. 111°. The *hydrochloride* is sparingly soluble. The oxidation to p-*tetra-anisyltetrazen*,

$$N_2[N(C_6H_4\cdot OMe)_2]_2,$$

could only be effected by means of *p*-benzoquinone. The tetrazen forms citron-yellow, four-sided plates, m. p. 117° (violent decomp.). Decomposition with acids gives the characteristic anisazonium compounds.

Tetratolyltetrazen dissolved in xylene, when heated for a few minutes, shows a violent evolution of nitrogen and formation of tetratolylhydrazine. E. F. A.

Catabolism of Proteins. FRANZ HOFMEISTER (*Arch. exp. Path. Pharm., Suppl.*, 1908, 273—281).—This paper is mainly a review of recent work on the cleavage of proteins, and the importance of such work and the necessity of dealing with pure substances are among the points insisted upon. W. D. H.

Effect of Acid and Alkali on the Osmotic Pressure of the Serum Proteins. L. ADAMSON and HERBERT E. ROAF (*Bio-Chem. J.*, 1908, **3**, 422—438).—Alkali increases (although not proportionally to the amount added) the osmotic pressure of the serum proteins. Acid causes this pressure to fall to zero, but larger amounts of acid increase it again. The point of zero pressure corresponds with the "alkaline reactivity" of serum ash. When the amount of alkali added is corrected by this "alkaline reactivity," the relationship of the osmotic pressure to the amount of alkali is a logarithmic one. The experiments with alkali are limited by the breaking up of the protein into particles small enough to pass a parchment paper membrane, and with acid by the partial precipitation of the protein. W. D. H.

Dissociation of Solutions of the Basic Caseinates [Caseinogenates] of Sodium and Ammonium. T. Brailsford Robertson (*J. Physical Chem.*, 1908, **12**, 473—483).—In a previous paper (Abstr., 1907, i, 1096), it has been shown that the solutions of sodium and ammonium caseinate neutral to litmus obey Ostwald's dilution law for binary electrolytes. Sackur (Abstr., 1903, ii, 4) had previously carried out electrical conductivity measurements with solutions of the corresponding "basic" salts, which were obtained by adding sufficient alkali to make the solutions neutral to phenolphthalein, the amounts of alkali required to produce the basic and neutral solutions being in the ratio 8 : 5. The author now shows from Sackur's results that the solutions of the basic caseinates also follow the dilution law for binary electrolytes, so that casein appears to behave as a monobasic acid in both solutions. Sackur has suggested that casein behaves to alkalis as a tetrabasic acid, but it is shown that the evidence for this view is untrustworthy.

The above results are best accounted for on the view that complex ions containing casein are present. The neutral caseinates are ampho-salts of the combined base, containing the ions $NaX^{\cdot}$ and $XXOH'$ (X = casein), whilst the basic caseinates are true salts of the combined base, the solutions containing the ions $Na^{\cdot}$ and $XXOH'$. In all the solutions there is an equilibrium of the type $NaX^{\cdot} + HXOH \rightleftarrows Na^{\cdot} + HXXOH$, which is not displaced by dilution.

From Sackur's results, the value $15 \cdot 2 \times 10^{-5}$ cm./sec. is obtained for the velocity of the casein ion in solutions of basic sodium caseinate, and $9 \cdot 1 \times 10^{-5}$ cm./sec. for the velocity of the same ion in solutions of ammonium caseinate.

The dissociation constants for the "basic" sodium and ammonium salts of casein are 0·0499 and 0·0404 respectively. G. S.

Action of Iron and of Heavy Metals [as Oxygen Carriers]. Vincenzo Cervello (*Arch. exp. Path. Pharm., Suppl.*, 1908, 107—109).—The oxidation of guaiacum resin is accelerated by the salts of heavy metals, and most of all by those of iron and copper. In the case of ferric salts, a partial reduction to the ferrous state occurs. The part played by iron as a constituent of hæmoglobin is discussed. G. B.

Urochrome. I. Hermann Hohlweg (*Biochem. Zeitsch.*, 1908. **13**, 199—204).—The pigment was prepared from human urine, which was made alkaline with calcium hydroxide, precipitated with calcium chloride, the filtrate neutralised with acid, and evaporated in a vacuum to a syrup ; after separation of the greater part of the salts, the syrup was diluted and shaken for several hours with animal charcoal, which absorbed the pigment, and from which it was afterwards removed by glacial acetic acid. From the solution thus obtained, it was precipitated by ether. The brown powder prepared in this way contained 8·22% of ash, and was soluble in water and methyl alcohol, but insoluble in strong ethyl alcohol and other organic solvents. Its spectrum showed no absorption bands, and it did not give the urobilin reaction with ammoniacal zinc chloride. It gave the

Garrod reaction with acetaldehyde and subsequent treatment with ammoniacal zinc chloride; also the Molisch reaction with α-naphthol.
S. B. S.

Urochrome. II. K. E. SALOMONSEN (*Biochem. Zeitsch.*, 1908, 13, 205—207).—The product was prepared by a slight modification of Hohlweg's method (preceding abstract). It was purified by conversion into its calcium salt. On treatment of an aqueous solution of the pigment with bromine in the cold, a yellow *bromo*-derivative was obtained, which was soluble in alkalis. On warming an aqueous solution of urochrome with bromine, a more vigorous bromination accompanied by oxidation takes place.
S. B. S.

Urochrome. III. STEFANO MANCINI (*Biochem. Zeitsch.*, 1908, 13, 208—214).—The bromo-derivative of Hohlweg and Salomonsen (preceding abstracts) was prepared by a modified method, unconcentrated urine being employed for the purpose. It was purified by dissolving in alkali, precipitating by acid, dissolving the substance thus obtained in water, and treating again with bromine. The doubly-refracting, yellow product thus prepared, when heated with zinc dust or calcium hydroxide, gives strong pyrrole reactions. Its composition corresponds approximately with the formula $C_{36}H_{41}O_{12}N_7Br_6$, which would be a bromo-derivative of $C_{36}H_{47}O_{12}N_7$. This is not far removed from the formula $C_{36}H_{43}O_{10}N_7$, which Thudichum ascribed to uromelanin. For it the name *uropyrryl* is proposed. By oxidation of crude bromouropyrryl with bromine water, oxalic acid, an oily acid, which gives the pyrrole reaction, and also, most probably, bromoanil were obtained. Neither oxalic acid nor bromoanil were obtained when a product, purified by repeated solution in alkali, re-precipitation with acids, and re-bromination, was employed. The relation of uropyrryl to urochrome is not yet ascertained.
S. B. S.

Hippomelanin. I. PETER RONA and O. RIESSER (*Zeitsch. physiol. Chem.*, 1908, 57, 143—153).—Hippomelanin, purified by Fürth and Jerusalem's method (Abstr., 1907, ii, 797), has been oxidised by a 3% solution of hydrogen peroxide containing a small amount (0·002%) of hydrochloric acid in solution. The total nitrogen of the aqueous solution was 7·5%, and the ammoniacal nitrogen 4·2%, that is, 56% of the total nitrogen present in the hippomelanin. Attempts were made to isolate the other nitrogenous products in the form of copper compounds. A copper derivative was obtained which was insoluble in alcohol and water. This contained a small amount of copper oxalate, but no other constituent was obtained in a pure form.

A copper derivative soluble in alcohol and water was also obtained. From this a *base*, which was precipitated by phosphotungstic acid, was isolated. The *hydrochloride* is readily soluble in water or alcohol. The *picrate* is deposited as an oil sparingly soluble in alcohol; the *picrolonate* is a deep red compound sparingly soluble in water, and the *platinichloride*, N = 16·14%, forms ochre-yellow prisms, m. p. 280°, insoluble in alcohol.
J. J. S.

Inosic Acid. CARL NEUBERG and B. BRAHN (*Ber.*, 1908, 41, 3376—3381. Compare Abstr., 1907, i, 1097).—It is pointed out that the sugar obtained by hydrolysing inosic acid cannot be *r*-arabinose, as stated by Bauer (Abstr., 1907, i, 1098). The authors confirm their view that it is *l*-xylose. They have obtained it in a syrupy form, have shown that it gives the pentose reactions, and that it is dextrorotatory. They further show that it does not yield a diphenylhydrazone as readily as does *r*-arabinose.

Levene and Jacob's conclusion (this vol., i, 931), that in place of a pentose inosic acid yields a tetrose-carboxylic acid, is shown to be untenable. J. J. S.

Glucothionic Acid. JOHN A. MANDEL and CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 13, 142—147. Compare Abstr., 1905, ii, 736).—Preliminary investigations show that the product obtained from the kidneys contains sulphuric acid in a conjugated form. Dextrose is not a product of hydrolysis, and neither is the substance of polysulphide nature. For these reasons, the name glucothionic acid is inapplicable. Names indicating the origin of the product are suggested, for example, *renosulphuric acid.* S. B. S.

Jecorin and other Lecithin-like Substances in the Liver of the Horse. A. BASKOFF (*Zeitsch. physiol. Chem.*, 1908, 57, 395—460).—Jecorin was prepared so that it gave a constant N : P ratio and a constant yield of sugar (about 14%). It is a diamino-monophosphatide in Erlandsen's sense.

The alcoholic extract of the liver is evaporated to a syrupy consistency, and treated with ether; a jecorin-like substance forms as a heavy layer at the bottom of the vessel; there is also a brown precipitate, insoluble in ether and alcohol, which was not further investigated. The addition of alcohol to the ether extract produces a precipitate of crude jecorin, lecithin remaining in solution. The precipitate is again treated with ether, and a jecorin-like substance remains insoluble; the extract, however, contains Drechsel's jecorin, which is precipitable by alcohol, and can be purified by the repetition of this process three or four times. W. D. H.

Glutamic Acid in Various Keratins. EMIL ABDERHALDEN and DÉNES FUCHS (*Zeitsch. physiol. Chem.*, 1908, 57, 339—341).—The following table gives the mean analytical results obtained, in parts %:

	Hoof of ox.		Horn of ox.		Hoof of horse.
	1 yr. old.	4 yrs. old.	1 yr. old.	4 yrs. old.	
Dry residue	90·5	91·5	96·0	96·5	75·4
Ash	0·14	0·16	0·22	0·36	0·45
Melanin substances	0·22	0·12	1·65	0·96	0·9
Glutamic acid hydrochloride in ash-free dry residue	18·0	16·8	13·8	12·9	18·2

Attention is called to the variable numbers obtained, and to the fall of glutamic acid and rise of ash with increasing age. W. D. H.

The Composition of the Protamine from Salmon Spermatozoa. Louis Nelson (*Arch. exp. Path. Pharm.*, 1908, **59**, 331—335).—The protamine was prepared by Schmiedeberg's method, and converted into the platinichloride. It was found that an impurity could be removed from the latter by hot water. The protamine was found then to have a composition corresponding with the formula $C_{16}H_{27}O_2N_9$.
S. B. S.

Chemistry of Protamines. I. Protamine from the Spermatozoa of the Caspian Sturgeon, Accipenser Guldenstädtii. W. D. Malenück (*Zeitsch. physiol. Chem.*, 1908, **57**, 99—112. Compare Kuraéeff, Abstr., 1901, ii, 462).—For isolating protamines and determining the yield, the method of precipitating with sodium picrate is preferred to Kossel's method of repeated solution of the sulphate in water and precipitation with alcohol. The sulphuric acid extract is stirred continuously with the aqueous picrate solution until a flocculent, orange-yellow precipitate is formed. The filtrate should be clear and free from opalescence, and should yield a further precipitate with sodium picrate. The precipitated picrate is washed, dried, dissolved in acetone, and decomposed with sulphuric acid. A portion of the picrate is insoluble in acetone, and this is shown to consist of adenine picrate, whereas the protamine picrate is readily soluble. In decomposing the acetone solution of the picrate, it is essential that an excess of sulphuric acid is not added.

The last traces of picric acid can be removed by solution in water, evaporating the solution, carefully precipitating with alcohol and acetone, and rubbing the sticky mass in a mortar with acetone until hard. The dry sulphate prepared by such a method usually contains only 0·3% of ash when dried at 108—110°, and gave the following analytical results: C, 37·64; H, 6·61; N, 20·92, and H_2SO_4, 22·59%. Similar data were obtained with a sulphate which had been converted into the chloride by Goto's method. The formula $C_{27}H_{55}O_7N_{13},2H_2SO_4$ agrees best with these data.
J. J. S.

Thymamine, a Protamine from the Thymus Gland. Louis Nelson (*Arch. exp. Path. Pharm.*, 1908, **59**, 336—340).—The protamine was prepared by extracting the coagulated proteins of the gland with copper chloride solution by Schmiedeberg's method, by means of which a solution of the hydrochloride is obtained. Sodium hydroxide is added until the reaction is neutral, and the filtrate from the precipitate thus produced evaporated, when copper protein combinations separate. The filtrate from these is diluted and evaporated, and more protein separates and is filtered off. These processes are repeated until a solution which no longer gives a reaction with Millon's reagent is obtained. The protamine is prepared from this by precipitating as phosphotungstate, and is finally obtained in the form of a platinichloride, the purification of which is described in detail. Its composition corresponds with the formula $C_{22}H_{40}O_5N_6$.
S. B. S.

The Action of Tyrosinase from Russula delica on Polypeptides which contain Tyrosine and on Suprarenine. Emil Abderhalden and Markus Guggenheim (*Zeitsch. physiol. Chem.*, 1908, **57**, 329—331. Compare this vol., i, 237).—In addition to the polypeptides previously used, tyrosinase rapidly splits *d*-alanyl-*l*-tyrosine and *l*-leucyl-*l*-tyrosine. It also decomposes suprarenine (adrenaline), with the rapid formation of a red colour, and later of dark-coloured flocculi; *l*-, *d*-, and *dl*-suprarenines are all decomposed with equal rapidity. W. D. H.

Milk Proteins and Enzymes. GEORGE A. OLSON (*J. Biol. Chem.*, 1908, **5**, 261—282).—After removal of the caseinogen and albumin, milk, cream, and butter are stated to yield a new protein, which is precipitable by hydrochloric acid. It contains 18·9% of nitrogen. When it is added to milk, it produces partial digestion of the caseinogen; this power is most active at 65°, and is destroyed at 80°. After removal of the new protein, the filtrate also has the same property; the ferment action of the protein is therefore believed to be due to incorporation. W. D. H.

The Scission by Diastase of Lactose, Maltose, and their Derivatives. H. BIERRY and J. GIAJA (*Compt. rend.*, 1908, **147**, 268—270).—The lactone of lactobionic acid was treated with macerations of fœtal intestines (sheep and oxen) and with digestive juices of snails. The former was inactive, whereas the latter caused the production of galactose; it also acts on lactosazone with the production of galactose. Similar results were obtained with the lactone of maltobionic acid. These facts afford further evidence of the specific nature of the ferments. S. B. S.

Action of Organo-magnesium Compounds on Arsenious Oxide. FRANZ SACHS and HANS KANTOROWICZ (*Ber.*, 1908, **41**, 2767—2769).—The addition of powdered arsenious oxide to an ethereal solution of magnesium phenyl bromide leads to the formation of diphenylarsine oxide after thirty minutes' heating, and of triphenylarsine after three hours. With magnesium *p*-tolyl bromide, only tri-*p*-tolylarsine is obtained, whilst with magnesium benzyl bromide, after three hours' heating, a *substance*, $As(CH_2Ph)_2 \cdot OH,H_2O$, m. p. 215—216°, is formed after the usual operations. C. S.

Triphenylstibine Sulphide. LUDWIG KAUFMANN (*Ber.*, 1908, **41**, 2762—2766).—Contrary to the statement of Michaelis and Reese (Abstr., 1886, 884), triphenylstibine sulphide can be prepared under the following conditions: Pfeiffer's triphenylstibine (Abstr., 1905, i, 164) is converted into a haloid additive compound, preferably the dibromide, which is dissolved in alcoholic ammonia, and hydrogen sulphide passed through the solution until a faint yellow coloration appears in the liquid; the crystals which have separated are recrystallised from alcohol, whereby colourless *triphenylstibine sulphide*, $SbPh_3S$, is obtained, m. p. 119—120°. Prolonged heating of its solutions or treatment with acids, even acetic, causes decomposition into sulphur and triphenylstibine.

If, during the preparation, the current of hydrogen sulphide is continued, the crystals redissolve to a yellowish-red solution, which probably contains a very labile antimony compound, for, by keeping, the liquid deposits sulphur, and the colourless filtrate, which is free from sulphur, yields pure triphenylstibine by evaporation. C. S.

Action of Grignard Reagents on Ethyl Orthosilicate. Eugen Khotinsky and Basile Seregenkoff (*Ber.*, 1908, **41**, 2946—2953).—When ethyl orthosilicate, dissolved in dry ether, is added gradually to a cold ethereal solution of a Grignard reagent, the mixture heated for ten to fifteen minutes on the water-bath, and decomposed by 50% acetic acid, compounds are obtained of the type $R\cdot Si(OEt)_3$. Only one ethoxyl group can be replaced (compare Tschitschibabin, Abstr., 1905, i, 283). If the heating is prolonged, or if excess of the Grignard reagent is used, complex silicon compounds are formed. In order to prevent the presence of any trace of moisture, the reaction is carried out in a current of dry hydrogen.

Ethyl orthosilicobenzoate, $SiPh(OEt)_3$, b. p. 232—234°, has been prepared by Ladenburg (*Annalen*, 1874, **173**, 151); it is hydrolysed by cold hydriodic acid, D 1·7, yielding Ladenburg's silicobenzoic acid, $C_6H_5\cdot SiO_2H$, m. p. 92°, which is also obtained when the reaction product of an excess of magnesium phenyl bromide and ethyl orthosilicate (1 mol.) is decomposed by sulphuric acid. By prolonged heating of the mixture before decomposition by sulphuric acid, trisilicobenzoylsilicic acid, $OH\cdot Si(O\cdot SiPhO)_3$, is obtained, which is also found in the high-boiling residue in the preparation of the ortho-ester; it appears to be identical with Polis' compound (Abstr., 1886, 618). *Ethyl ortho*-2 : 4-*dimethylsilicobenzoate*, $C_6H_3Me_2\cdot Si(OEt)_3$, b. p. 268—271°, obtained in a similar manner from magnesium *m*-xylyl iodide, yields, by hydrolysis, the *acid*, $C_6H_3Me_2\cdot SiO_2H$, m. p. 118—121°. The residue in the distillation of the ester contains *trisilico-xylyloylsilicic acid*, $Si(O\cdot SiO\cdot C_6H_3Me_2)_3\cdot OH$, an infusible, non-volatile, greyish-white powder.

Ethyl α-orthosiliconaphthoate, $C_{10}H_7\cdot Si(OEt)_3$, has b. p. 293—295°, and yields, by hydrolysis with cold hydriodic acid, *α-siliconaphthoic acid*, $C_{10}H_7\cdot SiO_2H$, m. p. 239°, softening at 225°, and, by hydrolysis with cold concentrated sulphuric acid, a *sulpho-α-siliconaphthoic acid*, $SO_3H\cdot C_{10}H_6\cdot SiO_2H$, m. p. 88—90°. *Ethyl β-orthosiliconaphthoate*, $C_{10}H_7\cdot Si(OEt)_3$, has b. p. 270—273°, and the *acid*, $C_{10}H_7\cdot SiO_2H$, m. p. 248—250°. C. S.

A Zirconium Mercury Double Salt. Walter Peters (*Ber.*, 1908, **41**, 3173—3175).—Although zirconium tetrachloride and mercury phenyl may be heated in a closed tube or under a pressure of 1 mm. without undergoing change, interaction takes place if the tube is evacuated by a water pump, owing to the presence of water vapour. The white, hygroscopic needles of the *salt*, $ZrOCl_2,2HgClPh$, are soluble in ether, and, when submitted to vacuum distillation at 170—210°, give a sublimate of mercury phenyl chloride and a residue of the composition $Zr_3O_4Cl_4,6HgClPh$. Mercury ethyl and mercury *o*-tolyl are without action. W. R

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